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VOLUME 10 MAY, 1934 NUMBER 5

THE EFFECT OF A MAGNETIC FIELD ON THE LINEAR RATE OF CRYSTALLIZATION[1]

BY E. W. R. STEACIE[2] AND C. F. B. STEVENS[3]

Abstract

An investigation has been made of the effect of a magnetic field of about 5000 gauss on the linear rate of crystallization from supersaturated solutions of sodium thiosulphate and nickel sulphate. The field had no appreciable effect in the case of sodium thiosulphate. Nickel sulphate showed a slightly increased rate of crystallization in the field.

Introduction

It would be anticipated that the rate of crystallization from a supersaturated solution would be affected by any factor which causes a change in the orientation of the molecules (or ions) of solute as they approach the interface. It is therefore of interest to investigate the effect of a magnetic field on the crystallization velocity, since no direct investigation has been made previously.

Kondoguri (1, 2) observed an increase in the rate of nucleus formation in the spontaneous crystallization of certain organic substances in a magnetic field. Roasio (3) found that in a field the growth of certain faces of several inorganic salts was favored, resulting in elongated crystals.

Apparatus

The main portion of the apparatus was a horizontal 5 ft. length of $\frac{1}{8}$ in. soft glass tubing, surrounded by a water jacket which could be maintained at constant temperature (20° C.). A hot saturated solution of the substance under investigation was sucked into the long tube and allowed to cool to the temperature of the water jacket. Crystallization was then induced by seeding at the open end.

[1] *Manuscript received April 3, 1934.*
Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Canada.
[2] *Assistant Professor of Chemistry, McGill University.*
[3] *Honors Undergraduate, McGill University.*

At one point the long tube passed between the poles of an electromagnet having pole pieces about 4 in. in diameter. The field strength was about 5000 gauss.

Rates of crystallization were determined by observing the time for the crystal boundary to advance through successive 5 cm. intervals.

The main difficulty encountered was the tendency for crystallization to start spontaneously at a number of places along the tube. It was found that this difficulty was very greatly accentuated if the tube were cleaned between runs with any powerful cleaning agent. On this account, therefore, only hot water was used. It was also essential that the solutions used should be free from dust, etc. They were therefore filtered through hot sintered Jena glass filters.

The rate of crystallization varied somewhat from tube to tube. In any run, however, the results were very consistent, and hence the effect of the field could be inferred accurately.

Experimental Results

I. *Sodium Thiosulphate*

The results of five typical runs are shown in Table I. In each case sodium thiosulphate crystals were dissolved in their own water of crystallization at 70° C., and then cooled to 20° C. in the tube.

TABLE I

SODIUM THIOSULPHATE

Interval in cm.	Time in seconds					Interval in cm.	Time in seconds					
	I	II	III	IV	V		I	II	III	IV	V	
0–5	150	116	190	209	149	55–60	157	133	181	190	155	
5–10	145	119	175	205	139	60–65	159	141	185	223	159	
10–15	149	130	188	199	133							
15–20	142	123	176	207	151	65–70	153	158	182	196	135↑	Field
20–25	147	123	184	205	144	70–75	150	125	181	212	141	
25–30	148	126	195	204	128	75–80	152	126	181	210	143	
30–35	156	137	180	205	137	80–85	150	125	180	213	143	
35–40	153	133	180	202	142	85–90	165	128	170	217	155↓	
40–45	148	127	180	204	140							
45–50	155	120	174	201	145	90–95	165	149	183	217	174	
50–55	155	135	180	200	159	95–100	170	163	188		145	
						100–105	163	150	185			
						105–110	146	130	184			
						110–115	145	123	180			

II. Attempts were also made to use supersaturated solutions of ferrous ammonium sulphate, ferric ammonium sulphate, ferric chloride, ferrous sulphate and nickel ammonium sulphate. In every case hydrolysis occurred to some extent, even if acid were added to check it. This resulted in a colloidal suspension which furnished an enormous number of nuclei and caused irregular crystallization all along the tube.

III. *Nickel Sulphate*

Experiments were also made with solutions of nickel sulphate. Great difficulty was encountered in preventing crystallization all along the tube, but a few successful runs were made. These showed widely varying rates of crystallization, but in any individual run the rate was reasonably constant. The data are summarized in Table II.

TABLE II

NICKEL SULPHATE

Saturated at	Cooled to	Supercooling, ° C.	Average rate, cm./min.	Average rate in field, cm./min.
29° C.	6° C.	23	0.436	0.472
80	6	74	0.036	0.045
50	8	42	0.083	—
82	6	76	0.057	0.065
82	3	79	0.021	—

It is evident that there is a slight acceleration in the field. The effect, however, is not much larger than the experimental error.

Discussion

The results indicate that there is very little alteration in the linear rate of crystallization in a magnetic field. It might have been anticipated that owing to the field certain orientations of a molecule or ion approaching a crystal would be favored. No such effect is noticeable. This fact may be considered to be additional evidence for the hypothesis that crystallization takes place by a preliminary adsorption followed by the incorporation of the adsorbed molecule or ion into the crystal lattice.

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A MATHEMATICAL TREATMENT OF A THEORY OF RUBBER STRUCTURE[1]

By T. R. Griffith[2]

Abstract

The theory that the elasticity of rubber is due to the heat vibrations of very long chain molecules, bound to one another at occasional points along their length, but able to move freely relatively to one another at all other points, is susceptible of mathematical treatment. In the present treatment it is assumed that the rubber molecule has a restricted rotation about the axis formed by joining two adjacent junction points.

A stress-strain curve has been developed mathematically on this assumption, and this curve, which is a reasonably close approximation to the curve obtained experimentally, serves as a standard with which to compare the rubber stress-strain curve and as a starting point for further mathematical work on the structure of rubber. The discrepancy between the mathematical and the experimental curve is explained on the very probable assumption that there is a wave motion or other vibration along the length of the rotating chain, as well as a rotation of the chain as a whole.

An explanation of the peculiar S-shape of the beginning of the experimental stress-strain curve develops automatically from the mathematically deduced relation between stress and strain, and it is also shown why the S-shape appears to vanish when the calculation of the stress is based on the actual cross section of the stretched rubber.

In addition, the following values, calculated from the above assumption and X-ray data, of certain constants, were obtained:

(i) The average distance between junction points.

(ii) The average length of molecular chain between junction points and, incidentally, the ratio between the number of freely swinging carbon atoms and those bound at junction points. This gives the number of freely swinging carbon atoms on the molecular chain between junction points and an idea of the length of the rubber molecule.

(iii) The quantity of kinetic energy per cubic centimetre causing the elastic effect in rubber.

(iv) The percentage of sulphur necessary to form the junction points in vulcanized rubber and, consequently, the minimum quantity of sulphur needed for vulcanization, both for hard and soft rubber. This minimum agrees closely with practical experiment.

A brief consideration of the work that has been done on the structure of rubber convinces one that the elasticity is wholly, or at least mainly, explained by a consideration of the kinetics involved.

The fact that when a strip of stretched rubber, one end of which is free, contracts when it is warmed, contrary to the behavior of most bodies, and that it becomes warmed on stretching, commonly known as the Gough-Joule effect (15, 19, 40, pp. 453–461), would lead one to suspect that there is a connection between the kinetic energy of the rubber molecule and its elasticity.

Lundal (25), Bouasse (7), Hyde (18), Somerville and Cope (34), Partenheimer (28) and Whitby and Katz (41) have reported observations, principally stress-strain curves, which show that vulcanized rubber has a lower modulus of elasticity at higher temperatures; *i.e.*, it becomes easier to stretch as the temperature is raised. On the other hand, Schmulewitsch (31), Stevens (37) and Williams (42) found that the elastic modulus increases with the temperature.

[1] *Manuscript received March 14, 1934.*
Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada.

[2] *Research Assistant, National Research Laboratories, Ottawa, Canada.*

Williams (42) shows that the softening of vulcanized rubber with rise of temperature is due to an increase of plasticity. In order to get rid of plastic flow, he first stretches the specimen several times to within about 50% of its breaking elongation, and then obtains an autographic stress-strain curve of the rubber stretched very quickly. He finds that in this case the rubber actually becomes stiffer with rise of temperature, increasing temperatures causing the stress-strain curves to lean progressively more and more towards the stress axis. He concludes that rise of temperature has two effects, one, a softening due to increase of plasticity, rendering plastic flow more easy, the other, an actual stiffening of the rubber due to rise of temperature. It is not easy to explain the latter effect on any theory which does not take kinetics into account.

It is difficult, for example, to explain the stiffening of rubber with temperature rise by means of the well known two-phase theory, which assumes both a liquid and a solid phase in rubber. In this connection Whitby (39) has shown that no liquid phase has ever been separated from rubber and that the so-called liquid phase which was supposed to be soluble in certain solvents shows the normal behavior of rubber. This phase is elastic, gives an X-ray pattern and will also vulcanize.

It has been shown first by Whitby (39) and later by Staudinger and Bondy (36) that the molecule of crude rubber exists in several different states of polymerization.

The needle molecule theory of Lindmayer (24), which assumes a needle-shaped molecule about 14 times as along as its diameter, as well as the theory which supposes the molecule to be in the form of a spiral (3, 12, 13, 21, 22), postulates a peculiar shape of the rubber molecule itself as the cause of the elasticity and other properties of rubber. In this connection Whitby (39) states that elasticity is shown not only by polymerized isoprene but by polymers of such widely different substances as methyl acrylate, styrene, vinyl acetate, sulphurized fatty oils, and by proteins, and that it can be caused to display itself in materials which are otherwise inelastic by the introduction of swelling agents or the application of heat. It is thus difficult to conceive how the elasticity of rubber can be due to a peculiar shape of the molecule. This shape would have to be the same in all these polymers if either of these theories were correct.

Shacklock (32) developed mathematically, from an assumed structure for rubber, a stress-strain curve which explains the peculiar S-shape of the stress-strain curve for rubber in a manner entirely different from that of the present article, but the development rests upon the assumption of an elastic fibril. The theory developed in the present paper shows how the elasticity of rubber evolves purely from the kinetic motions of the molecules, their inherent stiffness and elasticity being neglected.

The theory of rubber structure mathematically developed in this paper is essentially that of Boggs and Blake (4), who describe rubber as a network of extremely long chains, each link in the chain being a C_5H_8 unit.

Although an exact knowledge of the actual manner of combination of the C_5H_8 units to form a straight chain formula is not essential to the mathematical development, Whitby (38) showed that there are several schemes possible and, in addition, gives strong experimental chemical evidence in favor of the straight chain, primary valence structural formula for rubber.

In vulcanized rubber, according to Boggs and Blake (4), these chains are bound to one another at points along their length by sulphur atoms. These investigators further assume that the parts of the molecular chains between junction points are in motion relatively to one another and that one of these motions is rotational. They also state that Hock (17) had previously explained the Joule effect on the basis of the orientation of the molecules. Hock, however, though the first investigator to employ kinetics and the orientation of molecules to explain certain phenomena shown by rubber, does not mention rotation of the molecular chain, so that the portion of the hypothesis dealing with rotation is original with Boggs and Blake.

Starting, then, with this hypothesis, the present mathematical development assumes that this rotation is essentially a rotation of the molecular chain as a whole about the axis joining adjacent junction points, that the centrifugal force will cause a tension in the swinging molecular chain, and that a calculable component of this tension will draw the adjacent junction points together. It is assumed that each junction point in the network structure of rubber is joined to all or most of the junction points in its immediate neighborhood through the network, and that consequently each junction point will be drawn simultaneously towards all other junction points around it. The structure of rubber can thus be pictured by imagining it to consist essentially of junction points, connected to one another through a network, and all tending to get closer together, each being prevented from getting too close to adjacent junction points by heat vibrations and by its attraction towards other junction points. An equilibrium is thus established, and the junction points then occupy positions in which the resultant force on them in all directions is zero. If this equilibrium position is disturbed the junction points will immediately, on release of the external stress, return to their former orientation in space, and the body will recover its former shape.

The centrifugal motion, however, is necessarily a restricted one, because there is not enough room for a chain to make a complete turn about its axis without colliding with neighboring chains. Though the rotation is restricted, the centrifugal forces in the rotating part of the chain will nevertheless persist, the chain working its way into the interstices of the structure, away from the axis of rotation, just as surely as if complete rotation were possible.

Boggs and Blake (4), in explaining the Joule effect on their hypothesis, state that "when rubber is stretched, the mechanically applied tension causes at least a partial orientation of the molecules, as is evidenced by the development of double refraction and an X-ray diffraction pattern.

"This orientation due to stretching results in a loss of kinetic energy in the individual molecules on account of the restriction of thermal motion, which instantly appears in the mass of rubber as heat. The other phases of the Joule effect are similarly explained. The retraction of stretched rubber allows the molecules again to assume their random thermal motion, and the energy absorbed in this is drawn from the surroundings by a cooling of the rubber. The application of heat to stretched rubber increases the tendency for molecular motion, which reduces orientation and shortens the rubber accordingly or increases the tension required to maintain the stretched condition."

An additional idea which might be introduced into this conception is that a portion of the energy of stretching does not appear as heat, but is changed into potential energy resulting from the new shape of the molecule. It will be shown later that the tension in a chain rotating about an axis will be increased when the junction points are moved farther apart, as in stretching. This increase in tension, caused by the change in the curvature of the rotating chain, involves an absorption of potential energy which will be given out as mechanical work when the specimen contracts under load, no transformation to thermal energy taking place in the process.

If the rubber were to contract under no load, *i.e.*, snap back to equilibrium, it is evident that this potential energy would be converted into heat energy and tend to heat the specimen. In contraction under no load, therefore, there would appear to be two opposing effects in rubber; a cooling effect due to absorption of heat in the return to random thermal motion, and a heating effect due to the release of potential energy as heat. A quantitative calorimetric measurement of the temperature change of rubber in retraction under no load would appear to be necessary to determine which effect is the greater. In this connection, Gerke (14) has made some interesting applications of the laws of thermodynamics to the Joule effect.

The addition of still another idea to the conception of Boggs and Blake (4) will complete the picture. Heating of the stretched specimen will cause an increase in the kinetic energy of rotation of the chain molecule about its axis, which is the line joining two adjacent junction points. This, as will be shown later mathematically, will cause an increase in the tension in the chain and then cause the junction points to come together along the line of the stress, *i.e.*, will cause the specimen to retract somewhat under constant load. Thus there are two effects of increase in temperature in stretched rubber: first, a tendency to retraction, as conceived by Boggs and Blake, due to the effect of heat in producing the irregularity of the unstretched state, where the molecular arc of rotation becomes bent and twisted into all sorts of shapes and forms; second, a tendency to retraction brought about by increased kinetic energy of rotation which causes increased chain tension. The latter is, apparently, much the greater of the two effects.

The slight cooling noticeable in rubber during the very first stages of stretching is probably the same effect as that observed in all bodies subjected to tension. In rubber, however, the Joule effect rapidly sets in and is sufficient to mask this cooling, so that a heating effect is observed.

Meyer, von Susich and Valkó (27) have recently brought forward a theory of elasticity bearing a similarity to the one just described. They assume that in elongated substances that have a tendency to contract, there are present extremely long primary valence chains which are oriented in the direction of stretching. An essential part of the heat content of these chains consists of movements of rotation and deformation of individual atomic groups perpendicular to the molecular axis, while the valence vibrations in the direction of the molecular axis have a relatively small heat content. These transverse movements lead to irregular impacts of individual chains perpendicular to the direction of elongation. This results in a pressure of repulsion at right angles to this direction, which in turn causes the tractive tension. The temperature coefficient of tension is shown to be in accord with this kinetic concept. It will be observed that their theory presumably postulates short molecular arcs and that in the mathematical development of the present theory, the idea of rotation of extremely long molecular chains about an axis formed by joining two adjacent junction points is stressed as the main cause of the elastic effect. It might also be mentioned that the length of, and the number of atoms in, the rotating part of the chain have been calculated mathematically in the present theory.

The enormous swelling of rubber immersed in solvents is explained by the present theory on the assumption that the swelling medium simply interposes itself between the junction points and pushes them farther apart, and (in vulcanized rubber) without disrupting the structure or disturbing the relative orientation of the junction points to each other until after prolonged immersion (5, 39, p. 45).

It should be borne in mind that the theory herein described assumes absolute freedom of movement between adjacent molecular chains at all points except where they are bound together. This means that rubber acts like a liquid throughout most of its structure, and the only part where it may be considered to be solid, or rigid, is at the junction points, where there is no relative motion between adjacent molecular chains. The junction points also move or vibrate relatively to one another. Thus rubber is only a pseudo-solid, its solidity or tendency to hold a definite shape being due only to the equilibrium position of the junction points. Soft rubber, therefore, in some of its properties, acts like a liquid of very low viscosity. This can be inferred from the rapidity with which rubber will snap back to its equilibrium position after being deformed. If the liquid part of the rubber were viscous it would return very slowly. An example of what high viscosity in a rubber structure will do may be found in synthetic dimethylbutadiene rubber (41), which is very sluggish in retraction after deformation, but which when heated to around 70°C. has plenty of snap. There is thus in the present theory a certain similarity to the two-phase theory, but in this case only one size of molecule is concerned in both the liquid and solid phases.

Carothers, Williams, Collins and Kirby (10), in an article on poly-chlorobutadiene, the new synthetic rubber, state that chloroprene polymerizes in two different ways. In one type of polymerization the chloroprene molecules

join on to one another at the ends and form a long chain. Elasticity does not develop, however, until the second type of polymerization, a cross linking of the chains, takes place.

Busse (9), in describing the structure of rubber, mentions cross linking by means of sulphur bonds in vulcanized rubber and by means of intertangling of molecules in crude rubber. He also states that the molecular chains are in thermal motion, without stressing any particular type of motion. He explains how this view agrees completely with the known behavior of rubber.

It would not appear, however, that intertangling alone could account for the cross linking effect in crude rubber. One must also assume the action of van der Waals' forces holding the molecular chains together at the points where, owing to intertangling, they are constantly in contact. A certain amount of intertangling should also exist in vulcanized rubber.

Shacklock (32) describes an experiment with oleyl chloride, sulphur chloride and glycerol which points fairly definitely to the existence of a network structure in elastic vulcanized oils*.

In any event it is apparent that many investigators of rubber structure believe the property of elasticity to develop as a result of cross linking of long molecular chains. The present theory merely adds to this conception the idea that elasticity is the direct effect of the thermal and, in particular, the rotational vibrations of such a network.

As already intimated, it is possible to work out the mathematical consequences of the present theory. What is original about the present mathematical method is that the stress-strain curve is developed from an assumed rubber structure, whereas all previous mathematical treatments of the stress-strain curve of which the writer is aware, with the exception of that of Shacklock (32), attempt to find an empirical formula to fit the experimental stress-strain curve (2, 16, 23). None of these attempts have thrown much light on the structure of rubber because it has been impossible to interpret the true meaning of the equations obtained. The present mathematical development, while not resulting in a formula which fits the stress-strain curve with the accuracy of empirically obtained equations, has nevertheless necessitated the working out of some very interesting constants, and the work has thus thrown considerable light on the structure of rubber.

Explanation of Mathematical Method and Discussion of Results Obtained

General

When a collision between two adjacent chains takes place, rotation will obviously stop for an instant and the tension due to rotation will be momentarily lessened. Immediately after the collision, however, the rotation will increase again and the tension will be resumed. The mathematics neglects this momentary cessation of rotation and η, the kinetic energy of rotation in the molecular chain, is that amount of energy which will account for the elastic effect, assuming the rotation to be continuous. η is, as it were, an average or, rather, equivalent value. Any error in the above assumption, however, will not affect the other constants.

**See footnote on page 520.*

Though wave or other motion along the chain will also be considered, rotation has been taken as the basis of the calculation, because it was thought that only a structure in which rotation was the principal feature could account for the high elongations observed in rubber. For example, Fig. 1 illustrates a wave motion along the molecular chain, the amplitude of which is advisedly shown as equivalent to that of a semicircle. Such an amplitude is well above the maximum amplitude possible in a wave-like structure, especially since the arc ADB, as will be shown later, contains as many as 216 freely swinging chain carbon atoms, and Fig. 7 shows how closely the atoms in rubber are packed.

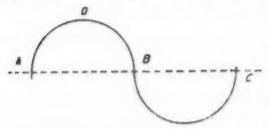

FIG. 1. *Semicircular molecular arc.*

The total possible elongation for the shape of arc given in Fig. 1 could not exceed 57.08%, as the following calculation will show:

$$\text{Elongation, \%} = \frac{100\,(\text{arc } ADB - AB)}{AB} = \frac{100\left(\frac{\pi AB}{2} - AB\right)}{AB} = 57.08\%,$$

assuming the arc ADB to be roughly a semicircle.

On the other hand, in Fig. 2, the arc FHG, rotating in a restricted manner about the axis FG, where F and G are junction points, could have any desired elongation, and shows closer packing; in addition, there is the possibility, as shown in the figure, of a wave motion along the rotating arc. For the sake of simplicity the first attack on the problem will ignore the wave motion, which will be used later to explain the small discrepancy between the calculated curve and that determined experimentally. Further work on this problem will have as its object the incorporation of rotation, wave motion and any other necessary corrections in the one equation relating stress and strain.

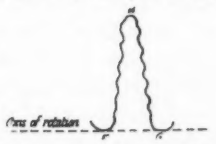

FIG. 2. *Postulated shape of molecular arc.*

Curve B, Fig. 8, was obtained by calculation, Curve A, with a specimen of rubber. Although the curves do not coincide, Curve B serves as a standard of comparison and as a first approximation. The preliminary work has, as already intimated, suggested a means of obtaining a closer approximation by incorporating wave motion. Doubtless still closer approximations will be attempted and obtained in the future until the rubber stress-strain curve is finally brought to an accurate mathematical basis.

Fig. 3 is a mathematical representation of a single rotating chain. The equation for this curve is worked out following the method of Appell and Lacour (1, p. 207-211) in their work on elliptic functions. OA_1O_1 is the molecular chain. O and O_1 are junction points with other molecular chains. The arc OA_1O_1 rotates about the axis OO_1. The distance OB_1 is ξ, the half-distance between junction points. The length of the arc OMA_1 is λ. Values for ξ and λ were obtained by equations worked out by the method of elliptic functions.

As, in order to relate stress and strain, the tension in the chain and the dimensions of the arc must be brought into the same equation, it was neces-

sary, using the general method of Appell and Lacour, to work out an equation for η, the total energy of rotation in the arc, this equation containing both these quantities. The following is the expression for η:

$$\eta = 4A\xi C, \tag{10}$$

where η is the energy in the length of arc, 2λ; A is the horizontal component of the tension in the arc, A being constant throughout the length of the arc; ξ is the distance OB_1, Fig. 3; and C, a variable dependent upon ξ and evaluated by tables of elliptic functions.

The equation for η expresses the value for η in terms of the dimensions of the arc and the tension in the chain, so that the problem then becomes one of expressing the arc dimensions in terms of the actual elongation of the rubber specimen, and the tension in the chain in terms of the stress in kilograms per square centimetre. To do this it is necessary to find, among other things ξ_o, the half-distance between junction points when the rubber is unstressed.

The mathematical artifice used to evaluate ξ_o is to suppose the rubber to be swelled to its maximum extent by, say, a solvent, so that all the molecular chains in the rubber are absolutely straight, and aligned along three axes at right angles to one another, each chain extending from one side of the cube to the opposite side. Every point at which it is possible for one chain to cross another in this system is then taken as a junction point. With the molecules thus regularly arranged it is an easy arithmetical calculation, knowing the total number of chain carbon atoms, and the distance between them from X-ray data (Fig. 7), to calculate the total number of chains, and, from that, the total number of junction points. The rubber is then assumed to contract to its original volume (1 cc.), when the straight chains form arcs owing to heat vibrations and draw the junction points to their normal distance apart in unstretched rubber, thus giving a figure for ξ_o. The degree of swelling permitted in this calculation is regulated by the maximum possible elongation, *i.e.*, the elongation at infinite stress or, rather, the elongation shown by the asymptote of the experimental stress-strain curve—in this particular case the asymptote, LM, of Curve A, Fig. 8. This maximum elongation was 850% and, therefore, the specimen was supposed to have to swell to an elongation of 850% in the directions of the three axes before the chains would be perfectly straight.

The fact that rubber does not swell to such an extent without disintegrating does not disprove the mathematical method. High internal stresses are involved in the swelling of rubber by solvents, and it is not surprising that rupture and disintegration should occur at an early stage of the swelling.

In the structure described above, stretching the rubber in only one direction does not straighten out all the arcs in that direction, those whose axes of rotation are at right angles to the direction of the stress not being appreciably extended. However, the chains on unextended arcs will also align themselves more or less in the direction of the stress, as do fillers which have definite crystallographic axes, thus explaining the X-ray results. Moreover, the

alignment of chains permits the van der Waals' forces to act, thus producing in the rubber a tendency to preserve this alignment, and reducing the tendency of the rubber to retract. This explains the phenomenon of hysteresis in vulcanized and crude rubber and also the phenomenon of racking.

Now the distance between junction points actually obtained by the mathematical artifice described above is that in an ideal soft vulcanized rubber, stretching to 850% along the three axes. In other words, a theoretical soft vulcanized rubber is being used as a basis of comparison.

The following general expression for ξ_o was found:

$$3.42 \times 10^{-7} \sqrt{\frac{x + 100}{src}} \text{ cm.}, \tag{16}$$

where x is the elongation at infinite stress, in this case 850%; s, the density of the rubber compound, 0.955; r, the percentage of crude in the mix, 93.11%; and c, the percentage of pure caoutchouc in the crude, 95.00% (11). The product, $src \times 10^{-4}$, is the weight in grams of pure caoutchouc in 1 cc. of compound.

The experimental mix used in obtaining the constants, x, s and r, indicated above, is shown in Table I.

TABLE I

RUBBER MIX USED FOR OBTAINING EXPERIMENTAL STRESS-STRAIN CURVE

—	Smoked sheets	Mercapto-benzo-thiazole	Sulphur	Zinc oxide	Stearic acid	Aldol-α-naphthy-lamine	—
Parts by weight	200	0.8	6	5	2	1	214.8
% of total	93.11	0.37	2.79	2.33	0.93	0.47	100.00

Minimum Quantity of Sulphur Required for Vulcanization—Soft Rubber

The total number of junction points in 1 cc. of rubber compound was found to be:

$$2.63 \times 10^{18} \left(\frac{src}{x + 100}\right)^{\frac{1}{2}} . \tag{17}$$

Giving the constants the values shown above, this becomes 6.98×10^{19}.

From this figure the quantity of sulphur necessary for vulcanization may be calculated. Assuming one atom per junction point, the vulcanization of the rubber to the ideal state indicated above would require 0.42% of sulphur in the rubber.

Boggs and Blake (4) state that about 0.5% combined sulphur is necessary and sufficient to produce soft vulcanized rubber. The close agreement between their figure and 0.42%, obtained on theoretical grounds, is more than a mere coincidence. The assumption of two atoms per junction point would make the calculated result 0.84%, which is too high, so that one sulphur atom per junction point is strongly indicated.

The combined sulphur content of the mix under observation, with which Curve *A*, Fig. 8, was obtained, was 2.70% and much higher than the above theoretical result, but a relatively high vulcanization temperature (141° C.) was used. Boggs and Blake (4) vulcanized in the cold, using an ultra accelerator. The much larger quantities of sulphur required in hot vulcanization can be explained by assuming that during hot vulcanization "two main factors are operative, namely: (i) a process of integration, pectization or 'firming up', which consists in (or goes hand in hand with) the chemical process of combination with sulphur, and (ii) a disintegrating or degradation process due to the heat as such." This is the conception of Schidrowitz and Goldsbrough (30). The conclusion to be drawn from such a conception is that if factor (ii) is absent, as in cold vulcanization, factor (i) does not have to proceed as far for complete vulcanization and less combined sulphur will be required.

Quite recently compounds for hot vulcanization have been developed, requiring less than 1% of vulcanizing agent, and it would appear that these compounds, which approach the mathematical ideal with respect to sulphur content, have improved physical properties. This has been shown by Booth (6) and by Somerville and Russell (35).

This explains why, in hot vulcanization, 2–5% of sulphur is needed, while in cold vulcanization about 0.5% may be sufficient. By the depolymerization, degradation, or increase in plasticity mentioned above, one understands on the present theory the breaking of molecular chains. Each break in the chain is mended by the formation of a sulphur bond at, or close to, the broken ends and each rupture requires extra sulphur. These bonds are, strictly speaking, not junction points, for they have freedom of movement, existing as they do on a rotating part of the chain. They might conceivably decrease plasticity somewhat. The calculated sulphur content is low because sulphur combined in this way is not taken into consideration in the calculation.

Minimum Quantity of Sulphur Required for Vulcanization—Hard Rubber

Another interesting calculation is the determination of the quantity of sulphur necessary to make rubber inextensible and inelastic. This is done by making x equal to zero in the expression for the total number of junction points, as follows:

$$2.63 \times 10^{18}\left(\frac{src}{0+100}\right)^{\frac{1}{3}} . \qquad (17)$$

When x is zero, according to the mathematical conception, the chains are stretched taut between junction points in the unstretched rubber.

Supplying one sulphur atom per junction point gives the value 11.6% for an inelastic compound containing rubber and sulphur only, which is considerably less than the possible maximum of combined sulphur, namely, 32%.

As the chains when in this state of relative immobility have, at room temperature, properties similar to those possessed by the molecules of a substance in the solid state, and as the junction points also form rigid connections between the chains at room temperature, the whole structure should

be solid at room temperature. However, at higher temperatures, owing to plastic flow in the junction points, such a structure may become softened. The question of plasticity will be further discussed later.

An experimental verification of this calculation would be difficult. To cause high percentages of sulphur to combine with the rubber, hot vulcanization is required, and while the 11.6% of sulphur was entering into combination at junction points, additional sulphur would be combining at the ends of broken chains to take care of depolymerization, so that the percentage of combined sulphur should be higher than 11.6% for an experimental compound at the point where the rubber just becomes solid and inelastic. It has just been shown that the calculation for soft rubber indicates 0.42% of sulphur at junction points when the corresponding experimental hot vulcanized sample had 2.70% of combined sulphur, or an excess of 2.20% to take care of depolymerization. The excess of 2.20% of sulphur (excluding that portion of the sulphur which combines with the other ingredients of the compound) serves in this case to join up the ends of molecular chains which have become severed through depolymerization. It is not unreasonable, therefore, to assume that when the sulphur at junction points reaches 11.6%, the total combined sulphur would have reached 17%, the point at which rubber is hard at room temperature (20).

The explanation of the apparent lowness of the mathematical result for combined sulphur in inelastic rubber is, therefore, quite simple, and the result does not cast doubt upon the accuracy of the mathematical method. The object having been to calculate the minimum amount of sulphur necessary to produce inelastic rubber, a higher result, say, one above 17%, would have been puzzling.

Apparent Molecular Weight of Rubber

The ratio of the total number of chain carbon atoms to the total number of junction points is 432, and as there are two chains passing through every junction point, each freely swinging arc has 216 chain carbon atoms, when x is 850%. Knowing that there are very many of these arcs in the single molecular chain, one sees in the mathematics a confirmation of the generally accepted view that rubber has a very high molecular weight.

This result also shows that by far the greater proportion of the internal structure of soft vulcanized rubber has the properties of a liquid and that only $\frac{2}{432} \times 100 = 0.46\%$ of its chain carbon atoms exist in a solid phase.

The great length of the molecular arc makes complete rotation around an axis impossible. The rotation under consideration must, therefore, be of an oscillatory or vibratory kind, with consequent twisting or deformation of the arc.

Equation Relating Stress and Strain

λ, the half-length, in centimetres, of the molecular chain between adjacent junction points, may be calculated from the fact that it becomes equal to ξ at maximum elongation.

F, the stress in kilograms per square centimetre, is obtained by multiplying A, the horizontal component of the tension in a single chain, by the number of chains per square centimetre, and converting the units from dynes to kilograms. The determination of the percentage elongation, ϵ, is also a simple arithmetical calculation from X-ray data, ξ and λ, and is given later. And now, knowing F and ϵ in terms of the variables used in the equation for η, the energy in the single arc, the following equation relating stress and elongation can be written—

$$F = \frac{\eta}{4.20 \times 10^{-16}\, C(\epsilon+100)}, \tag{26}$$

where C and ϵ are interrelated, C being obtainable by reference to the tables of elliptic functions. Curve B, Fig. 8, is drawn from this equation.

η cannot be calculated from atomic data, and consequently its value has been ascertained by supplying in the above equation known values of F and ϵ from the experimental curve. It is the only constant obtained in this way.

One reason why η is assumed to remain constant during stretching is that the atoms whose rotational motion resists the applied stress are moving virtually at right angles to the direction of the stress. Such being the case the stress has no effect upon their rotational motion or rotational energy. Thus the energy stored in the rotating arc by the separation of junction points is essentially potential in nature and not kinetic, and does not affect the value of η.

On rapid stretching the energy created by simplification of structure has no chance to become dissipated into the atmosphere. A stiffer stress-strain curve should result therefore, from this cause as well as from the fact that there is less time for plastic flow. On slow stretching, where there is time for the elimination of heat, however, η should remain more or less constant, and as the rate of stretching for the experimental Curve A, Fig. 8, was at the slow rate of 20 in. per minute, η is assumed constant in the present calculation.

Elastic Energy in Rubber

The value of η was found to be 7.12×10^{-12} ergs. η represents the energy in a complete chain, or 216 chain carbon atoms. Knowing the total number of chain carbon atoms in 1 cc., it is easy to calculate the total energy of rotation in 1 cc., which is 9.94×10^{8} ergs, or 24 gram calories. Assuming an approximate heat capacity of 0.47 cal. per cc. per degree (42, p. 872), this value is approximately equivalent to the amount of heat necessary to raise the temperature of the rubber 51° C. and, very roughly,

$$\frac{51}{293} \times 100 = 17\% \tag{31}$$

of the heat necessary to raise the temperature of the rubber from absolute zero to room temperature. Therefore, very roughly, 17% of the total heat energy in rubber is used in producing elasticity.

Although the above constant is only approximate, and necessarily depends on the correctness of the assumptions, nevertheless one is struck with the enormous possibilities of valuable information concerning the structure of rubber which can result from the application of mathematics to the problem.

Agreement of Stress-Strain Equation with Joule Effect

It is evident from Equation (26) that an increase in η, due to rise in temperature, would increase F for a given value of ϵ, C remaining constant when ϵ is constant. This explains why a specimen held extended under a constant load contracts when heated. The equation is thus in accord with the Joule effect. F, representing the internal stresses in the specimen resisting deformation, opposes, and is in equilibrium with, the constant load. An increase in F would result in a differential force causing the specimen to contract, and the contraction would continue until F, which naturally decreases with the contraction of the rubber, became equal to the constant load. Conversely, cooling would cause an increase in the elongation of the specimen under constant load.

Further, as η should be proportional to the temperature of the rubber, if ϵ is kept constant, making C constant, F for a given elongation should be a straight line function of temperature, provided that plasticity in the rubber can be eliminated.

The S-shape of the Stress-Strain Curve

Curve B, Fig. 8, has been drawn by means of Equation (26). It will be noticed that F becomes zero only when ϵ becomes equal to -100%. The significance of this is that, mathematically, the force of attraction between two adjacent junction points becomes zero only when the distance between them becomes zero, which is the case when ϵ equals -100%, whereas actually in rubber there is a definite distance between junction points, equal to $2\xi_o$, at zero stress. This is due to the fact that the junction points themselves repel one another owing to heat vibrations transmitted through the structure when they are close together and this repulsion balances the attraction between them at 0% elongation.

An attempt to formulate an equation passing through the origin has been made as follows. It is assumed that when junction points separate along the line of the stress they approach one another in a direction at right angles to the stress, because, the volume of the rubber remaining practically constant during stretching, the junction points must occupy a constant volume. Now, as the structure of the rubber is, as previously mentioned, liquid in nature, pressures in this medium are transmitted in all directions. Thus will the attraction between junction points at right angles to the direction of the external stress, owing to rotation, be transmitted as a sort of liquid pressure to the direction parallel to the stress, and tend to separate the junction points in the latter direction, thereby assisting the deforming stress. At 0% elongation, where the junction points are equidistant, there is an equality of junction point pressure in all directions, just balancing the attraction due to rotation,

and the resultant force on the junction point is zero. However, when the orientation is disturbed by deformation there is a greater force attracting the junction points in the external stress direction than at right angles to the stress, and the resultant force resisting deformation is the difference between the attraction, parallel to the stress, between junction points, due to rotation, and the attraction due to rotation at right angles to the stress. An equation to represent this condition has been developed as follows:

$$F_r = F_l - F_c = \frac{\eta}{4.20 \times 10^{-16}\, C_l(\epsilon_l+100)} - \frac{\eta}{4.20 \times 10^{-16}\, C_c(\epsilon_c+100)} \tag{28}$$

where

F_l is the stress in kilograms per square centimetre caused by junction point attraction parallel to the external stress,

F_c is the stress in kilograms per square centimetre caused by junction point attraction at right angles to the external stress,

F_r is the resultant stress resisting deformation, equal to $F_l - F_c$,

ϵ_l is the percentage elongation of the specimen, parallel to the stress, and therefore the elongation used in drawing the stress-strain curves,

ϵ_c is the percentage elongation of the specimen, at right angles to the stress. Naturally, as ϵ_l increases ϵ_c decreases and is always less than 0%. ϵ_c is calculated from ϵ_l from the fact that the junction points always occupy a constant volume.

C_l is the elliptic function corresponding to, and depending on, ϵ_l,

C_c is the elliptic function corresponding to, and depending on, ϵ_c.

Curve *C*, Fig. 7, has been drawn from this equation. It will be noticed that the stress becomes zero when the elongation becomes zero but, unlike the experimental curve, it has no S-shape.

As the junction points move farther apart in the direction of stretch they approach one another at right angles to this direction. A calculation was made to determine at what elongation the junction points came within the distances between chains, measured transversely to the stress, shown in the Meyer and Mark X-ray diagram, Fig. 7. It was found that this occurred at 1960%, indicating that at no time, even at the ultimate elongation, do the junction points approach very close to one another and that there are always a number of chain molecules between them. It is not likely that the liquid pressure mentioned above could be transmitted from junction point to junction point with a large number of chains intervening, and as the junction points move farther apart in the direction of stretch, the effect of transverse junction point pressure in assisting the stress would gradually disappear. The second part of Equation (28) would then become negligible and this equation would become similar to Equation (26). Thus there is a point where the curve of Equation (28) should merge into the curve of Equation (26), giving an S-shape.

It is difficult, in view of the fact that the Schopper machine on which the experimental sample was tested is not very accurate at low elongations, to

state just where the merging occurs. This point, however, has been determined experimentally for a pure gum compound by Shacklock (32), who finds "the inflexion point" at the "correct" cure to be at 72% elongation, and one concludes that the second part of Equation (28) disappears above 72% elongation, or long before any considerable relative displacement of junction points takes place.

Another way of considering this phenomenon, and possibly a better one, is to suppose the rubber specimen to be contracting. During the contraction, above 72%, Curve *B* is followed. Then at 72% the retracting junction points begin to get within the range of one anothers' influence, and begin to push one another apart at right angles to the external stress, thus decreasing their tendency to retract in the direction of the stress, so that Curve *B*, instead of continuing down to −100% elongation, becomes deflected to the point of zero stress and zero elongation. The experimental Curve *A*, if continued down to −100% elongation would lose all trace of an S-shape. This is true not only of Curve *A*, but of all experimental stress-strain curves for rubber, however compounded.

Hatschek (16) stated that by correcting for the diminution in area of cross section of the test piece, during extension, the point of inflexion disappeared. Shacklock (32), who made an accurate study of the stress-strain curve at low elongations, finds that the S-shape is still noticeable even when the stress is expressed as the force per unit of actual cross section.

It is not difficult to understand why the S-shape should become less apparent when the correction for the diminution in area of cross section is made. As the test piece becomes stretched the cross section diminishes, and the load, corrected for actual cross section, is thus greater than it would be were it calculated on a constant unit cross section. The calculated Curve *B*, Fig. 8, for example, if corrected, would cross the uncorrected Curve *B* at 0% elongation and lie closer to the elongation axis between −100% and 0% elongation, and closer to the stress axis above 0% elongation, than the uncorrected curve, *i.e.*, the slope to the stress axis above 0% elongation would decrease. Now, as already stated, the actual stress-strain curve is one which starts at zero elongation and zero stress and joins on to the calculated curve at around 72% elongation. It is apparent that a curve starting from the origin would merge the less abruptly into the calculated curve the less its slope at the point of merging. Thus any factor which decreases the slope of the stress-strain curve to the stress axis, such as correcting for actual cross section, or, for that matter, the addition of stiffeners to the rubber compound, will tend to make the S-shape less noticeable. This statement receives ample verification in actual experiment and it is well known that the S-shape is more apparent in the stress-strain curves of pure gum compounds than in heavily loaded compounds.

Thus the mathematics evolves from a well known theory of rubber structure a feasible explanation of the peculiar S-shape of the stress-strain curve for

rubber and shows why this S-shape becomes less apparent when the calculation of the stress is based on the actual cross section.

Means of Improving the Accuracy of the Calculated Stress-Strain Curve

In spite of the fact that Curves A and B have been made to agree as closely as possible at infinite stress and to coincide at 158% elongation (the value of η having been calculated from the value of F at the latter elongation), the calculated curve is stiffer than the experimental. In other words, in rubber there is a greater elongation produced by a given stress than can be calculated from rotation alone. This may be taken as strong evidence that there is a wave motion along the chain, and that the additional elongation caused by a given stress in the experimental curve is due to the unwinding of the wave motion along the molecular chains, which takes place along with the separation of the junction points.

The incorporation of wave motion into the equation relating stress and strain would take the form of a correction in the elongation. First of all, x, the elongation at infinite stress, must be reduced so that when the addition is made to the elongation to take care of wave motion, the calculated curve will coincide with the experimental at high elongation. Corrections will also have to be made all along the curve. While these corrections may easily be made empirically, an attempt to find a theoretical basis for them would undoubtedly be better.

The experimental Curve A, Fig. 8, is the curve obtained during the first stretching of the rubber specimen. It has long been known (8) that if rubber is stretched to a point fairly close to its breaking elongation and then allowed to retract, a further stretching yields a stress-strain curve closer to the elongation axis than the first one. The stress-strain curve for the next stretching is still closer to the elongation axis, and so on until a point is reached where only relatively slight changes in the position of the stress-strain curve are produced by further stretching. As the structure of fatigued rubber has greater permanency than that of unstretched rubber, it might be thought advisable to adopt the stress-strain curve of fatigued rubber or the reversible curves of Williams (42) or Gerke (14) instead of Curve A in the present instance. The objection to this procedure, however, is that continued stretching leaves the rubber in an anisotropic condition, owing to plastic flow, or other reasons. As in the mathematics a perfectly regular orientation of the structure is assumed, with the junction points ranged evenly along the three axes of reference, it was considered better to adopt the stress-strain curve produced by the first stretching as being more typical of isotropic rubber.

In the mathematics the network is assumed to be oriented along three axes at right angles to one another, one of the axes being parallel to the stress, which is actually, of course, not the case. However, as the value of η was obtained by supplying experimental values of F and ϵ in the equation relating stress and strain, η becomes the energy of arc which would give the above

values of F and ϵ, assuming a regularly oriented structure. The more exact calculation of η would encumber the mathematics considerably, and, in any case, such a procedure is quite unnecessary in a first approximation.

It is obvious, in view of the fact that vulcanized hard and soft rubber undergo plastic flow under stress at ordinary and at elevated temperatures, that the sulphur cross linkages are not unbreakable and that they can shift their position, giving permanent set. As vulcanized rubber, in common with crude rubber and other elastic polymers, exhibits plasticity, there is apparently no essential difference, except one of degree, among all elastic polymers. The chief reason for the superiority of vulcanized rubber is probably in a somewhat tighter, though still plastic, cross linkage bond, situated at the sulphur atom. Whitby (39) has expressed the view that the essential process in the development of elasticity in all elastic polymers, including vulcanized rubber, is a polymerization. This view is in no way opposed to the theory brought forward in this paper, where an attempt is made to show on physical grounds what kind of polymerization exists in vulcanized rubber, and to present a picture of its structure.

In making further corrections to the calculated stress-strain curve the effect of the change in structure actually taking place during the stretching, *i.e.*, the effect of such factors as plastic flow and breaking up of junction points should be considered as well as the effect of wave motion.

The expressions which have been worked out for the constants being of a general nature, the numerical values of x, s, r and c not having been filled in, these constants may be corrected as soon as a more accurate value for x has been obtained.

As the discrepancy between the calculated and experimental curves does not exceed 65% on the elongation axis at any point, it is seen that the errors in the constants caused by the neglect of wave motion and plastic flow in the calculations are not of serious proportions and not sufficient to alter any conclusions which have been drawn from the present results. In addition to this it has been shown that the rotation theory leaves a stress-strain curve closely approximating that for rubber, and it is doubtful whether any of the other existing theories would stand up as well if it were possible to work out their mathematical consequences.

Mathematical

The following development of a formula for the skipping rope curve is taken from a treatise on elliptic functions by Appell and Lacour (1, p. 207-211).

The rotating part of the rubber molecule, which is assumed for present purposes to be homogeneous along its length, will be on a curve in which there is equilibrium between centrifugal force and tension in the molecule.

The centrifugal force acting outwards on an element of mass, m, is perpendicular to the axis of rotation. Its intensity is $m\omega^2 r$, ω representing the

angular velocity of rotation and r the distance of the element, m, from the axis. Taking Ox (Fig. 3) as the axis of rotation, the problem may be briefly stated as follows.

A cord is attached at two points to the axis Ox and each element of the cord is repelled by the axis by a force proportional to the length of the element and to its distance from the axis.

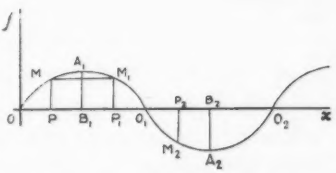

FIG. 3. *Skipping rope curve.*

As all the forces acting on the cord meet the axis Ox, the moment of the tension about this axis is constant throughout its length but, as the cord is attached to the axis at two points, the moment of the tension at the ends is zero. This moment is, therefore, zero throughout the axis, and introducing the z axis to take care of the general case where the arc is not in the vertical plane, the following equation for the moment is obtained:

$$T\left(y\frac{dz}{ds} - z\frac{dy}{ds}\right) = 0\,,$$

whence

$$\frac{dy}{y} - \frac{dz}{z} = 0\,, \quad y = mz\,,$$

m being a constant. The equilibrium diagram is, therefore, in a plane passing through the axis. Let us call this the xy plane, the force per unit length, Y, acting on the element, ds, being perpendicular to Ox, repulsive and proportional to the y ordinate. Thus

$$Yds = \mu y ds\,,$$

where μ is a constant and equal to $q\omega^2$, q being the mass per unit length of the molecule and ω the angular velocity.

The equations of equilibrium are, then,

$$d\left(T\frac{dx}{ds}\right) = 0\,, \qquad d\left(T\frac{dy}{ds}\right) + \mu y ds = 0\,,$$

the first giving

$$T\frac{dx}{ds} = A\,,$$

where one can always suppose A positive by computing the arc length, s, in such a way that x increases with s. A is the horizontal component of the tension, T. Using this value of T in the second equation and making

$$\frac{dy}{dx} = y'\,, \frac{\mu}{A} = \frac{2}{a^2}\,, \quad ds = \sqrt{1+(y')^2}\,dx = \frac{dy\sqrt{1+(y')^2}}{y'}\,,$$

the following equation is obtained:

$$\frac{y'dy'}{\sqrt{1+(y')^2}} + \frac{2ydy}{a^2} = 0\,,$$

and, on integrating,

$$\sqrt{1+(y')^2} + \frac{y^2}{a^2} = \frac{b^2}{a^2}\,,$$

b^2 representing a constant necessarily positive since the first member is positive. Isolating the radical, squaring, and substituting for y' its value, $\frac{dy}{dx}$, gives:

$$dx = \pm \frac{a^2 dy}{\sqrt{(b^2-y^2)^2-a^4}}. \qquad (P)$$

As the rope is attached to the axis, Ox, the equation should give a real value for y' when $y=O$; whence $b^2>a^2$. Designating by $\phi(y)$ the polynomial under the radical,

$$\phi(y) = (b^2+a^2-y^2)\ (b^2-a^2-y^2)\,.$$

y, starting from zero, can vary only between $-\sqrt{b^2-a^2}$ and $+\sqrt{b^2-a^2}$. In the construction of the curve let it be supposed that the cord is attached at O (Fig. 3) and that it is situated in the angle yOx; then x increases with y, $\frac{dy}{dx}$ is positive, and

$$x = \int_o^y \frac{a^2 dy}{\sqrt{\phi(y)}}; \qquad (Q)$$

while y increases, x increases, until $y=\sqrt{b^2-a^2}$; x then has the value:

$$\xi = \int_o^{\sqrt{b^2-a^2}} \frac{a^2 dy}{\sqrt{\phi(y)}}. \qquad (R)$$

The branch OA_1 is thus obtained, the tangent at A_1 being horizontal. Then y decreases, and in order that x may continue to increase, it is necessary to put the minus sign in front of $\sqrt{\phi(y)}$. Thus there is obtained a new branch, $A_1M_1O_1$, symmetrical to the first, OMA_1, with respect to the ordinate, A_1B_1, because equal variations in x correspond to equal variations in y. At the point O_1, $y=0$, and the abscissa is 2ξ. Then y, becoming negative, decreases until it reaches the value $-\sqrt{b^2-a^2}$; the abscissa increases again to the value 3ξ, which gives the point A_2, where the tangent is horizontal. Then y increases again from $-\sqrt{b^2-a^2}$ to $+\sqrt{b^2-a^2}$. After the value A_2 it is necessary to put the plus sign before the radical, the arc $A_2O_2A_3$ thus being obtained, cutting the axis at the point O_2 where the abscissa is 4ξ, and so on. The curve branches thus obtained are successively all equal to the first. The curve is thus analogous to a sinusoidal curve.

The following substitutions may now be made in Equation (Q):

$$y = t\sqrt{b^2-a^2},\ k^2 = \frac{b^2-a^2}{b^2+a^2} < 1\,,\quad 1-k^2 = (k')^2 = \frac{2a^2}{b^2+a^2}\,. \qquad (1)$$

Equation (Q) now takes the form:

$$\frac{x\sqrt{2}}{ak'} = \int_o^t \frac{dt}{\sqrt{(1-t^2)\ (1-k^2t^2)}}\,.$$

As this equation now has the form of Legendre's standard elliptic integral of the first kind, it may be represented, by the customary notation, as follows:

$$t = \operatorname{sn} \frac{x\sqrt{2}}{ak'}, \quad y = \sqrt{b^2 - a^2} \operatorname{sn} \frac{x\sqrt{2}}{ak'}.$$

Thus the curve gives a graphical representation of the variation of the sn function.

The differential, ds, of the arc of the curve is

$$ds = \sqrt{1 + \left(\frac{dx}{dy}\right)^2} \cdot dy.$$

By substituting in this equation the value for $\frac{dx}{dy}$ obtained in Equation (P),

$$ds = \frac{(b^2 - y^2)\, dy}{\sqrt{\phi(y)}},$$

and

$$s = \int_0^y \frac{(b^2 - y^2)\, dy}{\sqrt{\phi(y)}}. \qquad (S)$$

By making Substitution (1) in Equations (Q) and (S) there is found for abscissa ξ at the point A_1, and the length, λ, of the arc OA_1, the two expressions:

$$\left.\begin{aligned} \xi &= \frac{ak'}{\sqrt{2}} \int_0^1 \frac{dt}{\sqrt{(1-t^2)(1-k^2t^2)}} = \frac{ak'}{\sqrt{2}} K, \\ \lambda &= \frac{a}{k'\sqrt{2}} \int_0^1 \frac{(1+k^2-2k^2t^2)\, dt}{\sqrt{(1-t^2)(1-k^2t^2)}}, \end{aligned}\right\} \qquad (2)$$

because the point A_1 is obtained by making $t=1$, or $y=\sqrt{b^2-a^2}$ in Substitution (1).

All the elliptic functions developed in the present work can be reduced to terms of the elliptic symbols K and E.

$$K = \int_0^1 \frac{dt}{\sqrt{(1-t^2)(1-k^2t^2)}}, \quad \text{or, if } t = \sin\phi,$$

$$K = \int_0^{\frac{\pi}{2}} \frac{d\phi}{\sqrt{1-k^2\sin^2\phi}}.$$

$$E = \int_0^1 \sqrt{\frac{1-k^2t^2}{1-t^2}} \cdot dt, \quad \text{or, if } t = \sin\phi,$$

$$E = \int_0^{\frac{\pi}{2}} \sqrt{1-k^2\sin^2\phi} \cdot d\phi.$$

In the tables of elliptic functions (29, 33) the values of K and E are given for the corresponding values of $\sin^{-1} k$.

When λ and ξ are given (λ being greater than ξ because the arc OA_1 is greater than its projection OB_1) the constants a and k^2 have only one system of values, under the condition $k^2<1$. In fact, by calculating $\lambda-\xi$ and $\lambda+\xi$ the following relation is obtained:

$$\frac{\lambda-\xi}{\lambda+\xi} = k^2 \frac{\int_0^1 \sqrt{\frac{1-t^2}{1-k^2t^2}} \cdot dt}{\int_0^1 \sqrt{\frac{1-k^2t^2}{1-t^2}} \cdot dt} \quad . \tag{3}$$

For $k^2=0$, the value of the second member is zero. As k^2 increases, the numerator obviously increases and the denominator decreases. Thus the ratio increases, and for $k^2=1$ the ratio is 1. This ratio, then, passes once and only once through the given value $\frac{\lambda-\xi}{\lambda+\xi}$. The constant k^2 has, therefore, one and only one value. Equation (2) for ξ thus gives a single value for a.

FIG. 4. *Waves in skipping rope curve.*

There are an infinite number of positions of equilibrium for the cord, assuming it to have a given length, l, and to be attached at the points, O and O_1, to the axis, Ox, Fig. 4. Let the length, OO_1, be α.

1. The cord has only a single wave between O and O_1. Then ξ is half of α, λ half of l. The quantities ξ and λ being known, the constant, k^2, has a single value given by Equation (3), and $a=\frac{\alpha\sqrt{2}}{2Kk^1}$.

2. The cord has two waves between O and O_1. Then $\xi=\frac{\alpha}{4}$, $\lambda=\frac{l}{4}$. k^2 has the same value as in the preceding case because $\frac{\lambda-\xi}{\lambda+\xi}$ has the same value, $\frac{l-\alpha}{l+\alpha}$, and $a=\frac{\alpha\sqrt{2}}{4Kk^1}$.

In general, if the cord has n waves between O and O_1, $\xi=\frac{\alpha}{2n}$, $\lambda=\frac{l}{2n}$; k^2 has always the same value, but $a=\frac{\alpha\sqrt{2}}{2nKk^1}$. There is, therefore, an infinity of positions of equilibrium, all of which pass through O and O_1. In the assumed structure for rubber there is only one wave between O and O_1.

In order to express stress in terms of strain in rubber it is necessary to find a relation between A and ξ. These quantities are brought together in the equation for the energy of rotation, which is developed, as follows, in a manner similar to that given by Appell and Lacour (1, p. 207-211).

The kinetic energy due to the velocity of rotation of a particle of length, ds, in the skipping rope is represented by $\frac{qds\omega^2y^2}{2}$. In this case, y, the distance of the particle, ds, from the axis Ox is the radius of rotation. ω, as before, is the angular velocity of rotation and q the mass per unit length.

The energy in the length of rope from O to A_1, Fig. 3, *i.e.*, in the length, λ, equals:

$$\frac{q\omega^2}{2}\int_o^{\sqrt{b^2-a^2}} y^2ds \quad .$$

As

$$ds = \sqrt{1+\left(\frac{dx}{dy}\right)^2}\,dy = \frac{(b^2-y^2)dy}{\sqrt{\phi(y)}},$$

then

$$y^2ds = \frac{y^2(b^2-y^2)dy}{\sqrt{\phi(y)}};$$

therefore, the kinetic energy in the complete arc, OA_1O_1, *i.e.*, in the length, 2λ, equals

$$\eta = q\omega^2\int_o^{\sqrt{b^2-a^2}} \frac{y^2(b^2-y^2)dy}{\sqrt{\phi(y)}}.$$

Substitution (1) gives:

$$\eta = \frac{\sqrt{2}q\omega^2a^3k^2}{(k')^3}\int_o^1 \frac{(1+k^2-2k^2t^2)t^2dt}{\sqrt{(1-t^2)\,(1-k^2t^2)}}. \tag{4}$$

The integral in Equation (4) may be simplified by expansion.

$$\int_o^1 \frac{(1+k^2-2k^2t^2)t^2dt}{\sqrt{(1-t^2)\,(1-k^2t^2)}} = (1+k^2)\int_o^1 \frac{t^2dt}{\sqrt{(1-t^2)\,(1-k^2t^2)}} - 2k^2\int_o^1 \frac{t^4dt}{\sqrt{(1-t^2)\,(1-k^2t^2)}}.$$

The problem is to express Equations (3) and (4) in terms of K and E so that the tables may be used in their evaluation. Starting with Equation (3), letting $t=\sin\phi$, and simplifying by expanding into partial fractions,

$$\frac{\lambda-\xi}{\lambda+\xi} = k^2\frac{\int_o^1 \sqrt{\frac{1-t^2}{1-k^2t^2}}\cdot dt}{\int_o^1 \sqrt{\frac{1-k^2t^2}{1-t^2}}\cdot dt} = k^2\frac{\int_o^{\frac{\pi}{2}} \frac{(1-\sin^2\phi)d\phi}{\sqrt{1-k^2\sin^2\phi}}}{\int_o^{\frac{\pi}{2}} \sqrt{1-k^2\sin^2\phi}\,.\,d\phi}$$

$$= k^2\frac{\int_o^{\frac{\pi}{2}} \frac{d\phi}{\sqrt{1-k^2\sin^2\phi}} - \int_o^{\frac{\pi}{2}} \frac{\sin^2\phi\,.\,d\phi}{\sqrt{1-k^2\sin^2\phi}}}{\int_o^{\frac{\pi}{2}} \sqrt{1-k^2\sin^2\phi\,.\,d\phi}}.$$

Now,

$$\int_o^{\frac{\pi}{2}} \frac{\sin^2\phi\,.\,d\phi}{\sqrt{1-k^2\sin^2\phi}}$$

may be simplified by expansion (29) to

$$\frac{1}{k^2}\int_0^{\frac{\pi}{2}} \frac{d\phi}{\sqrt{1-k^2\sin^2\phi}} - \frac{1}{k^2}\int_0^{\frac{\pi}{2}} \sqrt{1-k^2\sin^2\phi}\,.\,d\phi$$

and this equals

$$\frac{K}{k^2} - \frac{E}{k^2}.$$

Therefore,

$$\frac{\lambda-\xi}{\lambda+\xi} = \frac{Kk^2-K-E}{E} = B. \tag{9}$$

By making $t=\sin\phi$ in the first partial fraction in Equation (4),

$$\int_0^1 \frac{t^2dt}{\sqrt{(1-t^2)(1-k^2t^2)}} = \int_0^{\frac{\pi}{2}} \frac{\sin^2\phi\,.\,d\phi}{\sqrt{1-k^2\sin^2\phi}}\,.$$

This, as has been shown in the evaluation of Equation (3), equals

$$\frac{K}{k^2} - \frac{E}{k^2}.$$

In the evaluation of the second partial fraction in Equation (4) the standard notation of Legendre is used. Let

$$\int_0^t \frac{dt}{\sqrt{(1-t^2)(1-k^2t^2)}} = u.$$

Then, if $t=\sin\phi$, $t=\mathrm{sn}\,u$. By using the method of elliptic functions, the following equalities may be derived by the substitution of sn u for t:

$$\int_0^1 \frac{t^2dt}{\sqrt{(1-t^2)(1-k^2t^2)}} = \int_0^K \mathrm{sn}^2u\,du = \frac{K}{k^2} - \frac{E}{k^2},$$

$$\int_0^1 \frac{t^4dt}{\sqrt{(1-t^2)(1-k^2t^2)}} = \int_0^K \mathrm{sn}^4u\,du.$$

For the evaluation of the integral, $\int_0^K \mathrm{sn}^4u\,du$ Appell and Lacour (1, p. 276-277) use an expansion of the expression, $\mathrm{sn}^{2n-3}\,u\ \mathrm{cn}\,u\ \mathrm{dn}\,u$, obtained by differentiating it according to the ordinary methods of calculus and then integrating, as follows:

$$\frac{d}{du}\left[\mathrm{sn}^{2n-3}u\,\mathrm{cn}\,u\,\mathrm{dn}\,u\right] = (2n-3)\,\mathrm{sn}^{2n-4}u\,(1-\mathrm{sn}^2u)\,(1-k^2\,\mathrm{sn}^2u) - \mathrm{sn}^{2n-2}u\,(1-k^2\,\mathrm{sn}^2u) - k^2\,\mathrm{sn}^{2n-2}u(1-\mathrm{sn}^2u),$$

or, on simplifying,

$$(2n-3)\,\mathrm{sn}^{2n-4}u - (2n-2)\,(1+k^2)\,\mathrm{sn}^{2n-2}u + (2n-1)\,k^2\,\mathrm{sn}^{2n}u.$$

On integrating,

$$\mathrm{sn}^{2n-3}u\,\mathrm{cn}\,u\,\mathrm{dn}\,u = (2n-3)\int \mathrm{sn}^{2n-4}u\,du - (2n-2)\,(1+k^2)\int \mathrm{sn}^{2n-2}u\,du + (2n-1)k^2\int \mathrm{sn}^{2n}u\,du.$$

Putting $n=2$ in this equation,

$$\operatorname{sn} u \operatorname{cn} u \operatorname{dn} u = \int du - 2(1+k^2)\int \operatorname{sn}^2 u\, du + 3k^2 \int \operatorname{sn}^4 u\, du \quad ,$$

whence

$$\int_0^K \operatorname{sn}^4 u\, du = \frac{1}{3k^2}\left(\Big[\operatorname{sn} u \operatorname{cn} u \operatorname{dn} u\Big]_0^K - \int_0^K du + 2(1+k^2)\int_0^K \operatorname{sn}^2 u\, du\right)$$

$$= \frac{1}{3k^2}\left(0 - K + 2(1+k^2)\left[\frac{K}{k^2} - \frac{E}{k^2}\right]\right) \quad .$$

The value of η can now be expressed in terms of K, E and k, as follows:

$$\eta = \frac{\sqrt{2}q\omega^2 a^3 k^2}{(k')^3}\left(\frac{K+E}{3} - \frac{K-E}{3k^2}\right) \quad .$$

The substitutions

$$q\omega^2 = \mu \quad , \quad a^2 = \frac{2A}{\mu} \quad , \quad a = \frac{\xi\sqrt{2}}{Kk'} \text{ (from Equation (2))} \quad , \quad a^3 = \frac{2\sqrt{2}A\xi}{\mu K k'} \quad ,$$

are useful in simplifying the equation for η.

$$\eta = \frac{4A\xi k^2}{K(k')^4}\left(\frac{K+E}{3} - \frac{K-E}{3k^2}\right) \quad .$$

Letting

$$\frac{k^2}{K(k')^4}\left(\frac{K+E}{3} - \frac{K-E}{3k^2}\right) = C \quad ,$$

$$\eta = 4A\xi C \quad . \tag{10}$$

The next step is to find a means of expressing A in terms of the stress on the rubber specimen in kilograms per square centimetre and ξ in terms of the percentage elongation.

Calculation of n

The present theory assumes the rubber structure to be made up entirely of swinging arcs in irregular arrangement. The arrangement is such that the arcs do not rotate in pairs on opposite sides of the same axis, although some of the arcs might take up this position. It is more probable that the adjacent junction points about which one arc rotates are formed by the union of three separate molecular chains. Thus there are three separate molecular chains for each pair of junction points, and the calculation is based on this type of structure.

In the calculation of the total number of junction points in rubber, they are supposed to be aligned along three co-ordinates parallel to the edges of the cube. While the structure has, strictly speaking, not this extreme regularity, the assumption is necessary for the mathematical development, the results justifying it.

The next step is to suppose the cube of rubber to be stretched along the three co-ordinates until the molecular arcs are perfectly aligned and lie evenly between their respective junction points. Fig. 5 shows a cubic lattice illustrating the transformed rubber structure, the lines representing molecular chains and the points where they meet, the junction points.

The degree of stretch along the three co-ordinates necessary to attain perfect alignment of molecular chains is taken as x, the percentage elongation represented by the asymptote, LM, to the experimental stress-strain curve (see Curve A, Fig. 8). This is called the elongation at infinite stress, a constant which figures considerably in the mathematical work.

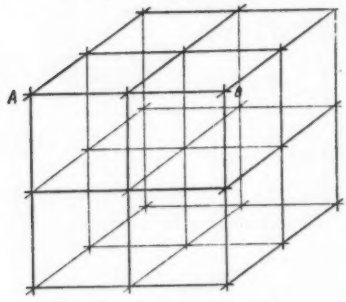

FIG. 5. *Cubic lattice used in calculations.*

The number of chain ends along any one of the edges, such as AB, of the cube in Fig. 5, being n, the total number of chains is $3n^2$ and the total number of junction points, n^3. However, as it is impossible for three chains to be joined together at one point, Fig. 6 gives a better idea of the true appearance of the rubber structure, where there are actually $2n^3$ junction points, there being two junction points now for every one represented in Fig. 5. The total number of chains remains the same, namely $3n^2$.

The reasoning prompting the drawing of Fig. 6 is based upon the assumption that it is impossible for one chain molecule to pass permanently into the territory of oscillation of another chain by crossing it at a sharp angle without forming a junction point with it at the point where they cross. Again, it is not possible for there to be more junction points than represented in Fig. 6, because the incorporation of more junction points into the figure than already shown would necessitate a reduction in x. Thus the mathematical artifice used for the calculation of the total number of junction points per cubic centimetre gives the maximum number of junction points for an elongation of x per cent at infinite stress. Fewer junction points than this would mean that the forces of attraction between molecular chains failed to act at points where they would be most likely to act (*i.e.*, where the chains crossed), which is improbable. The basis of the calculation, therefore, in addition to being justified by the results obtained, is in itself not unreasonable.

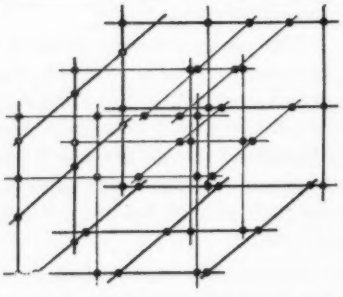

FIG. 6. *Postulated structure of distended rubber, showing junction points.*

In the calculation of the total number of junction points on one chain (each chain assumed to extend from one side of the cube to the opposite side), it must be borne in mind that each junction point exists on two chains. There are $2n^3$ junction points, each affecting two chains, and there are $3n^2$ chains. Thus the total number of junction points on one chain equals

$$\frac{2 \times 2n^3}{3n^2} = \frac{4n}{3}.$$

As previously stated, 1 cc. of rubber compound contains $src \times 10^{-4}$ gm. of pure rubber. The molecular weight of the C_5H_8 unit being 68.06, and the mass of the hydrogen atom 1.66×10^{-24} gm. the actual weight of a C_5H_8 unit is

$$\frac{68.06 \times 1.66 \times 10^{-24}}{1.008} \text{ gm.}$$

The number of C_5H_8 units in 1 cc. of rubber compound is, therefore, the weight of pure rubber in 1 cc. of compound divided by the weight of a C_5H_8 unit, or

$$\frac{src \times 10^{-4} \times 1.008}{68.06 \times 1.66 \times 10^{-24}} = 8.92 \times 10^{17}\, src.$$

As one of the carbon atoms in isoprene is on a side chain, there are only four chain-forming carbon atoms per isoprene unit. Therefore, the number of chain-forming carbon atoms in 1 cc. of rubber compound is

$$4 \times 8.92 \times 10^{17}\, src = 3.57 \times 10^{18}\, src. \tag{11}$$

The length of 1 cc. of rubber after being stretched $x\%$ will be $\frac{(x+100)}{100}$ cm. Assuming the rubber to be stretched to this extent along three axes at right angles to one another, all the chains will be perfectly aligned along the three axes, as illustrated in Fig. 6. The distance between carbon atoms along the chain is best obtained by the use of X-ray data. In Fig. 7, due to Meyer and Mark (26), it will be observed that the chains are aligned along the c-axis of the unit cell and that there are eight carbon atoms in the cell distance of 8.1×10^{-8} cm. The distance between neighboring carbon atoms along the chain is, therefore,

$$\frac{8.1 \times 10^{-8}}{8} = 1.01 \times 10^{-8} \text{ cm.}$$

The total number of carbon atoms in a complete chain, *i.e.*, in a distance of $\frac{(x+100)}{100}$ cm. is $\frac{(x+100)}{100 \times 1.01 \times 10^{-8}} = \frac{(x+100)}{1.01 \times 10^{-6}}$.

The division of the total number of chain carbon atoms by the item just obtained gives the total number of chains in 1 cc., each chain being equal in length to the distance between opposite faces of the distended cube.

$$\frac{3.57 \times 10^{18}\, src \times 1.01 \times 10^{-6}}{(x+100)} = \frac{3.61 \times 10^{12}\, src}{(x+100)}.$$

This figure is the total number of chains in 1 cc., and as the chains are assumed to be aligned parallel to the three axes, the number of chains aligned parallel to any one axis is one-third of this figure, or

$$\frac{1.20 \times 10^{12}\, src}{(x+100)}. \tag{13}$$

The number of chain ends along any one of the edges of the cube, or n, is the square root of item (13).

$$n = \sqrt{\frac{1.20 \times 10^{12}\, src}{(x+100)}} = 1.10 \times 10^{6} \sqrt{\frac{src}{(x+100)}}. \tag{14}$$

Calculation of ξ_o

The number of junction points on each chain is, as previously calculated, $\frac{4n}{3}$, or

$$1.46 \times 10^6 \sqrt{\frac{src}{(x+100)}}. \tag{15}$$

The number of junction points per chain was calculated by postulating an imaginary condition of the rubber where a cube is distended to the geometrical limit. The present theory assumes that there are as many junction points in rubber in the natural, unstretched state as there are in this imaginary distended state. In the normal state, since the calculations are being made on 1 cc. of rubber compound, the distance between chain ends is 1 cm., and for the purposes of the calculation the junction points are still assumed to lie on lines parallel to three co-ordinates at right angles to one another and parallel to the sides of the cube. The distance, therefore, between adjacent junction points on the same chain when the rubber is at 0% elongation is the reciprocal of item (15), and equals

$$2\xi_o = \frac{1}{1.46} \times 10^{-6} \sqrt{\frac{(x+100)}{src}};$$

$$\xi_o = 3.42 \times 10^{-7} \sqrt{\frac{(x+100)}{src}}. \tag{16}$$

ξ_o, as previously stated, is the value of ξ when the rubber is at zero per cent elongation. It equals 1.15×10^{-7} cm. for Compound *A*.

Minimum Percentage of Sulphur Required for Vulcanization—Soft Rubber

The present theory assumes that at the junction points there is a cross linking of molecular chains through the agency of sulphur atoms. Knowing the total number of junction points per cubic centimetre of compound, one may, assuming a sulphur atom at each junction point, calculate the minimum amount of sulphur necessary for vulcanization. As the values of x, s and r for Compound *A* will be used, the result of the calculation will be the minimum quantity of sulphur of vulcanization necessary to give an elongation at infinite stress of 850% in a typical pure gum stock. The result may also be interpreted as representing the quantity of sulphur, out of the total of 2.79% actually incorporated into Compound *A*, serving to form the junction points in this compound.

Now, the total number of junction points in 1 cc. is $2n^3$, and from Equation (14),

$$2n^3 = 2.63 \times 10^{18} \left(\frac{src}{x+100}\right)^{\frac{3}{2}} = 6.98 \times 10^{19}. \tag{17}$$

The weight of a sulphur atom is

$$\frac{32.06 \times 1.66 \times 10^{-24}}{1.008} = 5.28 \times 10^{-23} \text{ gm.}$$

The percentage of junction point sulphur, calculated on the crude rubber in the mixing, in 1 cc., or 0.955 gm. of compound, is

$$\frac{5.28 \times 10^{-23} \times 6.98 \times 10^{19} \times 100}{0.93 \times 0.955} = 0.42\%.$$

The calculation of this figure as a percentage of the whole mix makes but little difference to the result, it being 0.39% in this case.

It is interesting to note that if the value of x were increased to 1100%, without changing any of the other quantities in this calculation, the percentage of sulphur would be reduced only to 0.30%.

Minimum Percentage of Sulphur Required for Vulcanization—Hard Rubber

In the calculation of the percentage of sulphur necessary to give inextensible and inelastic rubber, a pure rubber-sulphur mix is used. The following values for s, r, c and x are supplied in the equation for the total number of junction points per cubic centimetre: $s=0.915$, the density of pure caoutchouc (11); $r=100\%$; $c=100\%$; $x=0\%$, giving the result, $2n^3=2.30 \times 10^{21}$. The total amount of sulphur necessary to place a sulphur atom at each one of these junction points equals $2.30 \times 10^{21} \times 5.28 \times 10^{-23}=0.12$ gm. The percentage of sulphur would be

$$\frac{0.12 \times 100}{0.915 + 0.12} = 11.6\%.$$

Calculation of Freely Swinging Arc—Soft Rubber

An interesting calculation may be made at this point; namely, the comparison of the total number of chain carbon atoms with the total number of junction points. This gives an idea of the amount of free chain in comparison with the amount of bound chain. Using the values of s, r, c and x for Compound A, the total number of junction points per cubic centimetre was calculated to be

$$6.98 \times 10^{19}. \tag{17}$$

The total number of chain forming carbon atoms equals

$$3.57 \times 10^{18} src = 3.02 \times 10^{22}. \tag{11}$$

Item (11) divided by item (17) gives the ratio:

$$432 \text{ chain carbon atoms per junction point.} \tag{18}$$

As each junction point accounts for a length of chain which is the equivalent of two complete arcs, the number of chain carbon atoms lying between two adjacent junction points is the half of item (18), or 216.

Calculation of Freely Swinging Arc—Hard Rubber

The calculation of the freely swinging arc depends upon the total number of junction points in hard rubber, which, as already shown, equals $2n^3=2.30 \times 10^{21}$, and which depends upon x, the elongation at infinite stress. When x decreases, the ratio of the total number of chain forming

carbon atoms to the total number of junction points also decreases, *i.e.*, the amount of free chain decreases, as would be expected. When x equals zero this ratio becomes

$$\frac{3.02 \times 10^{22}}{2.30 \times 10^{21}} = 13.1. \tag{19}$$

Hence, there are approximately seven chain carbon atoms between adjacent junction points when x equals zero. According to the mathematical conception these seven carbon atoms exist in a chain which is stretched taut between junction points.

Relation Between ξ and ϵ

ϵ, the percentage elongation of the specimen, is given by the equation:

$$\epsilon = \frac{100(\xi - \xi_o)}{\xi_o}.$$

Hence

$$\xi = \frac{\xi_o(\epsilon + 100)}{100}. \tag{23}$$

Calculation of λ

When ϵ equals x, the molecular chain is stretched taut between the junction points, and $\xi = \lambda$, the half length of the molecular chain. Making these substitutions in the equation for ϵ, given above,

$$x = \frac{100(\lambda - \xi_o)}{\xi_o}.$$

Hence

$$\lambda = \frac{\xi_o(x + 100)}{100}.$$

Substitution of the value of ξ_o, obtained in Equation (16), gives:

$$\lambda = 3.42 \times 10^{-9} \frac{(x + 100)^{\frac{1}{3}}}{(src)^{\frac{1}{3}}}.$$

Relation Between A and F

It will be remembered that A is the horizontal component of the tension in the single molecular chain. F, being the stress on the specimen in kilograms per square centimetre, is equal to the sum of all the horizontal components, A, in a square centimetre of cross section at right angles to the direction of stretching. Thus F, divided by the number of chains per square centimetre, as given in item (13), and converted to dynes, equals A.

$$A = \frac{1000 \times 980\, F(x + 100)}{1.20 \times 10^{12}\, src} = 8.15 \times 10^{-7} F \left(\frac{x + 100}{src}\right).$$

Stress-Strain Curve Equation Beginning at -100% Elongation

By substituting the values, just obtained, for A and ξ in the equation:

$$\eta = 4A\xi C, \tag{10}$$

and giving ξ_o the value shown in Equation (16), η may be expressed in terms of stress in kilograms per square centimetre and percentage elongation.

$$\eta = 1.12 \times 10^{-14} FC(\epsilon + 100)\left(\frac{x + 100}{src}\right)^{\frac{1}{3}} \text{ ergs.} \tag{24}$$

Giving x, s, r and c the values which they have in Compound A, the equation becomes:

$$\eta = 4.20 \times 10^{-16} FC(\epsilon + 100) \text{ ergs,} \tag{25}$$

or

$$F = \frac{\eta}{4.20 \times 10^{-16} C(\epsilon + 100)} . \tag{26}$$

Stress-Strain Curve Beginning at 0% Elongation

Equation (28), mentioned earlier in this paper, which gives a stress-strain curve beginning at 0% elongation, is deduced by assuming the junction points to occupy a constant volume. In this way, the relation between ϵ_l, the percentage elongation in the direction of the stress, and ϵ_c, the percentage elongation, corresponding to ϵ_l, at right angles to the stress, may be found. ϵ_c, the cross sectional elongation, is always less than 0%, and is a measure of the contraction of one of the sides of the cross section square consequent upon stretching the specimen to an elongation ϵ_l. Letting ξ_l represent the half junction point distance in the direction of the stress and ξ_c the half junction point distance at right angles to the stress,

$$(\xi_o)^3 = \xi_l(\xi_c)^2 .$$

It is evident from Equation (23) that

$$\xi_l = \frac{\xi_o(\epsilon_l + 100)}{100} ,$$

and

$$\xi_c = \frac{\xi_o(\epsilon_c + 100)}{100} .$$

The substitution of these values in the above equation for $(\xi_o)^3$ gives:

$$\epsilon_c = \frac{1000}{\sqrt{\epsilon_l + 100}} - 100 . \tag{27}$$

Since arc rotation causes all the junction points to be attracted towards one another, the average attraction, A_c, between any two adjacent junction points in a plane at right angles to the stress, will be transmitted through the structure as a kind of hydrostatic pressure and tend to force apart the junction points along the line of the stress, thus diminishing A_l, the average force of attraction between any two adjacent junction points along the line of the stress. The average force resisting deformation, therefore, is a differential force, $A_l - A_c$, which is represented in Equation (28)

$$F_r = F_l - F_c = \frac{\eta}{4.20 \times 10^{-16} C_l(\epsilon_l + 100)} - \frac{\eta}{4.20 \times 10^{-16} C_c(\epsilon_c + 100)} . \tag{28}$$

The meaning of the symbols has already been given. Since F_l and F_c are proportional to A_l and A_c, it has not been found necessary to incorporate the latter two symbols into this equation. ϵ_l and ϵ_c have the relation indicated in Equation (27).

Calculation of Elongation at which the Junction Points Approach within X-ray Distances

As the junction points move farther apart in the direction of stretch they approach one another at right angles to this direction. A calculation will

now be made to determine at what elongation the junction points come within the distances between chains, measured transversely to the stress, shown in the Meyer and Mark X-ray diagram, Fig. 7. These distances are:

$$\frac{12.3}{2} = 6.15\,\mathring{A}, \quad \text{and} \quad \frac{8.30}{2} = 4.15\,\mathring{A} .$$

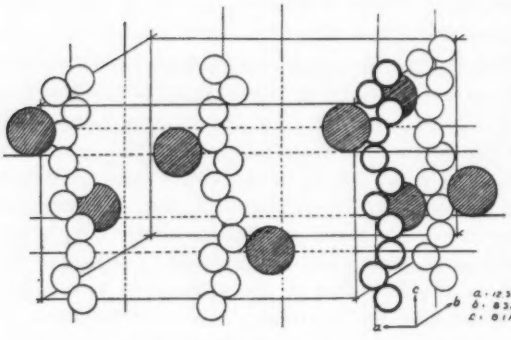

FIG. 7. *Spacing of rubber molecules according to Meyer and Mark (26), obtained from X-ray data. White circles represent carbon atoms and hatched circles represent CH_2 groups.*

The elongation at this point is found by assuming that the cell bounded by eight adjacent junction points has a constant volume, equal to $(2\xi_o)^3$. Letting y represent the distance between adjacent junction points along the line of the stress at the elongation to be calculated, $(2\xi_o)^3 = y \times 6.15 \times 10^{-8} \times 4.15 \times 10^{-8}$; therefore,

$$y = \frac{(2\xi_o)^3}{6.15 \times 4.15 \times 10^{-16}},$$

and the percentage elongation equals

$$\frac{100(y-2\xi_o)}{2\xi_o} = \frac{100y}{2\xi_o} - 100 = \frac{100(2\xi_o)^3}{6.15 \times 4.15 \times 10^{-16}} - 100 = 1960\% .$$

Calculation of η

The average value of η was calculated by supplying in Equation (26) a value for F at 14.8 kgm. per sq. cm., obtained from experimental Curve A, Fig. 8, at $\epsilon = 158\%$. As F and ϵ are known, and as C can be calculated from ϵ by a method given later, η can be found, and has a value of 7.12×10^{-12} ergs. This is the elastic energy in a single arc.

Substitution of this numerical value of η in Equation (28) gives the following result:

$$F_r = F_i - F_c = 1.69 \times 10^4 \left(\frac{1}{C_i(\epsilon_i + 100)} - \frac{1}{C_e(\epsilon_e + 100)} \right) , \tag{32}$$

and, above 72% elongation:

$$F = \frac{1.69 \times 10^4}{C(\epsilon + 100)} . \tag{33}$$

These equations are represented graphically in Fig. 8. Curve A is the stress-strain curve drawn from an actual specimen, Curve C was obtained from Equation (32), and Curve B from Equation (33). Comments on these curves have already been made.

Calculation of the Elastic Energy per Cubic Centimetre in Rubber

When the values of x, s, r and c for Compound A are used, the single arc contains, as shown in Calculation (18), 216 chain carbon atoms, and this length of arc has, as shown above, 7.12×10^{-12} ergs of elastic energy. There

being, according to Calculation (11), 3.02×10^{22} chain carbon atoms in 1 cc. of rubber compound, the total elastic energy in 1 cc. equals:

$$\frac{7.12 \times 10^{-12} \times 3.02 \times 10^{22}}{216} = 9.94 \times 10^{8} \text{ ergs} = 24 \text{ gram-calories},$$

or, approximately, as previously explained in Calculation (31), 17% of the total heat energy in the rubber.

Relation Between C and ϵ

Now

$$\epsilon = \frac{100(\xi - \xi_o)}{\xi_o}$$

and

$$x = \frac{100(\lambda - \xi_o)}{\xi_o} ,$$

therefore, by algebra,

$$\frac{\epsilon + 100}{x + 100} = \frac{\xi}{\lambda} .$$

But

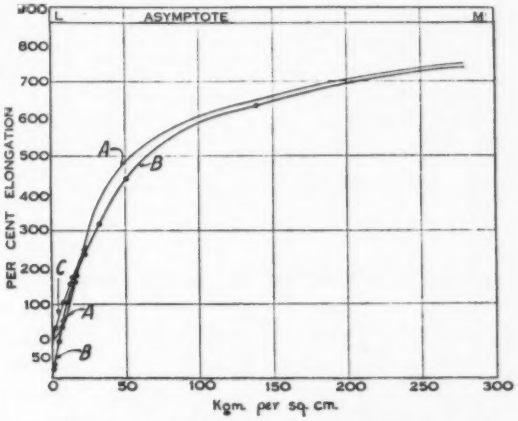

FIG. 8. *Experimental and calculated stress-strain curves. A—Experimental curve. B—Calculated curve, Equations (26) and (33). C—Calculated curve, Equations (28) and (32).*

$$\frac{\xi}{\lambda} = \frac{1 - B}{1 + B}, \quad \text{because} \quad \frac{\lambda - \xi}{\lambda + \xi} = B \quad ; \tag{9}$$

therefore,

$$\frac{\epsilon + 100}{x + 100} = \frac{1 - B}{1 + B}, \quad \text{and} \quad \epsilon = (x + 100)\left(\frac{1 - B}{1 + B}\right) - 100 \quad . \tag{34}$$

Now, when k is given, both K and E are fixed, and since both B and C Equations (9) and (10) are functions of k, K and E, as shown in Calculations (9) and (10), the values of B and C are fixed by the value of k. Again, if x is constant, which is the case for any one mix and cure, ϵ, according to Equation (34), is a function of B, so that ϵ is also fixed when k is given. Thus there is a definite value of C to correspond to each value of ϵ, this being the value for which k is the same in both of these functions.

In the tables of elliptic functions (29, 33) are given the values of K and E to correspond to values of $\sin^{-1}k$, in increments of 1°. These increments being fairly large sometimes require an interpolation to obtain intermediate values. In the case of Equation (33), where it was necessary only to find a number of points sufficiently close together to draw a curve, the procedure was to choose arbitrarily various values of k, obtain the corresponding values of K and E from the tables of the elliptic functions, then calculate ϵ and C, and, by putting these values of ϵ and C in the equation, obtain F, which gave a point on the stress-strain curve. Table II gives the results of the calculations that were made in this connection.

In the case of Equation (32) however where, incidentally, the value of k for C_l and ϵ_l is different from its value for C_c and ϵ_c, interpolation was necessary. Arbitrarily chosen values of k gave, as above, values of ϵ_l and C_l; then ϵ_c was calculated from ϵ_l by Equation (27), and the value of C_c, to correspond to ϵ_c obtained, through interpolation, by means of a chart (Fig. 9). C_l, ϵ_l, C_c and ϵ_c being known, the value of F_r could be calculated and a point on the curve obtained, F_r in this case being plotted against ϵ_l. There being, as already explained, a definite value of C for each value of ϵ, negative values of ϵ were plotted against the corresponding values of C to obtain the curve in Fig. 9. These values were taken from the ϵ_l and C_l columns in Table II.

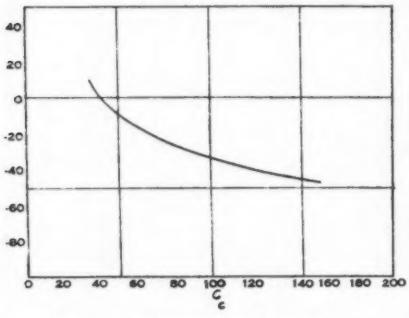

FIG. 9. *Chart relating C_c and ϵ_c.*

All the calculations are tabulated in Table II, and the stress-strain curves shown in Fig. 8 were drawn using the values given in this table. Although the second part of Equation (32) is supposed to disappear above 72% elongation, where Equation (33) is applicable, the values of F_c and F_r in Table II carry Equation (32) to 244% elongation.

TABLE II

CALCULATED VALUES OF ELONGATION AND STRESS USING THE METHOD OF ELLIPTIC FUNCTIONS

$\text{Sin}^{-1} k$	$\frac{1-B}{1+B}$	ϵ_l	C_l	ϵ_c	C_c	F_l	F_c	F_r
0°	1.000	850	0.0000	—	—	∞	—	—
10	.969	822	.0207	—	—	889	—	—
20	.885	740	.0717	—	—	281	—	—
30	.757	619	.200	—	—	118	—	—
40	.603	474	.499	—	—	59.2	—	—
50	.442	320	1.28	—	—	31.4	—	—
55	.362	244	2.17	−46	160	22.7	2.0	20.7
60	.286	172	3.91	−39	120	15.9	2.3	13.6
61	.272	158	4.44	−38	116	14.8	2.4	12.4
65	.215	104	7.73	−30	89	10.7	2.7	8.0
67	.189	79	10.5	−25	76	9.0	3.0	6.0
69	.163	55	14.7	−20	66	7.4	3.2	4.2
70	.151	43	17.6	−16	58	6.7	3.5	3.2
73	.116	10	32.1	− 5	44	4.8	4.1	0.7
74	.105	0	40.1	0	40	4.2	4.2	0.0
75	.0943	−11	50.8	—	—	3.7	—	—
76	.0841	−20	65.6	—	—	3.2	—	—
77	.0750	−29	86.2	—	—	2.8	—	—
78	.0650	−38	116	—	—	2.4	—	—
79	.0569	−46	160	—	—	2.0	—	—
80	.0479	−54	227	—	—	1.6	—	—
85	.0146	−86	3010	—	—	0.4	—	—
86	.00995	−91	6900	—	—	0.3	—	—
90	.00000	−100	∞	—	—	0.0	—	—

Conclusion

The inferences drawn from the mathematical results have been given at the beginning of the article. This order of presentation was thought to be the best, because the thread of the mathematics might be lost if the development were interrupted by lengthy comments.

To sum up, it may be stated that the mathematical consequences of a well known theory of rubber structure, the theory which assumes rotation in the long molecular chain, have been worked out, with results showing surprisingly close agreement with experiment. The correctness of the rotation theory is thus well demonstrated, in addition to which certain constants are developed which throw further light on the structure of rubber.

Acknowledgments

The author wishes to express his gratitude to Dr. G. S. Whitby, Director, Division of Chemistry, National Research Council, for his continued interest in the work. He is also indebted to C. R. Boggs, Vice-President, Simplex Wire and Cable Company, to Donald W. Kitchin of the same company, and to R. H. Gerke of the United States Rubber Company, for helpful criticisms of the manuscript.

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Additional references (see p. 491) showing the general trend of opinion toward a tri-dimensional network in vulcanized rubber are given below.

H. Staudinger, (Revue Générale du Caoutchouc, 8 : 7-75. 1931.) states that tri-dimensional reactions leave rubber insoluble. If these reactions are not extensive, as in soft vulcanized rubber, it can swell considerably, but if they are extensive, as in hard rubber, there is no swelling.

J. D. Lang, W. E. Singer and W. P. Davey, (Ind. Eng. Chem. 26 : 543-547. 1934.) consider rubber to be a tangle of spiral or zigzag molecules or molecular complexes.

THE ALKALOIDS OF FUMARIACEOUS PLANTS

IX. *DICENTRA FORMOSA*, Walp.[1]

By Richard H. F. Manske[2]

Abstract

In addition to the hitherto known alkaloids of *Dicentra formosa* (protopine, dicentrine), the present investigation has disclosed the presence of glaucine and corytuberine as well as alkaloid δ which had previously been obtained from *D. eximia*. Heyl's alkaloid of unknown identity (m.p. 142° C.) proved to be corydine. Incidentally, the author's eximine was also identified with corydine.

The object of the chemical investigations named in the above title is the elucidation of a number of problems regarding this Botanical Family*, the wider scope of which it is hoped will lead to an understanding of the biogenesis of the alkaloids. As a preliminary, however, it is essential to include in this study not only a large number of species, but to examine each as thoroughly as possible. As will appear in the sequel the re-examination of *Dicentra formosa* on this basis was warranted.

The alkaloids of this plant have been examined by Heyl (5) who demonstrated the presence of protopine and two other bases which were regarded as new. In a later examination of *Dicentra pusilla*, Asahina (1) isolated a base which he named dicentrine and which proved to be identical with one of Heyl's alkaloids. Heyl's third alkaloid (m.p. 142.5° C.) was regarded by Späth, Mosettig and Tröthandl (9) as possibly identical with the *d*-tetrahydropalmatine which these authors had found in *Corydalis tuberosa*. Support was given to this supposition by the fact that both bases exhibited the phenomenon of triboluminescence.

It seemed highly improbable, however, that but three bases should be elaborated by this plant when other species belonging to the same family are usually more liberal as to variety. In view of the development of a more adequate procedure for dealing with such refractory mixtures of alkaloids (7), a re-investigation was undertaken, and it was hoped that the exact identification of Heyl's alkaloid would be possible.

The results of the present investigation fully confirm those of Heyl. Protopine and dicentrine were readily isolated, and in a state of purity. The alkaloid melting at 142° C.† proved to be phenolic, and careful comparison disclosed its identity with the alkaloid previously isolated from *D. eximia* (8) and named eximine. Both products furthermore exhibit the characteristic violet triboluminescence.

[1] *Manuscript received April 18, 1934.*
Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada.

[2] *Chemist, National Research Laboratories, Ottawa.*

**The writer's attention has been drawn to the fact that the name Order or Natural Order is now generally applied to a much more comprehensive group of superior rank than the word Family which is used to designate those groups of genera of a closer botanical association. Chemists have not generally adopted this nomenclature. In order, however, to arrive at a common usage, that of the botanists will be used subsequently, even though there may be some confusion for a time.*

†*Melting points are corrected.*

In the meantime, however, the chemical examination of eximine has disclosed its identity with an alkaloid obtained from *D. canadensis* (6) and which at that time was regarded as identical with corydine. This identity has been further confirmed by comparison with an authentic specimen of *d*-corydine, which melted at 140-141° C., and for which the author expresses his indebtedness to Professor Ernst Späth. The optical activity is approximately that recorded by Gadamer (3) for *d*-corydine, and methylation with diazomethane has yielded *d*-corytuberine dimethyl ether, characterized as the *l*-bitartrate. Finally, racemization, by oxidation with iodine and subsequent reduction, yielded an inactive base melting at 168° C. Gadamer records the melting point of *dl*-corydine as 165–167° C. (? corr.).

As far as the author is aware the tribolumescent property of corydine is not a matter of previous record. That it is due to the corydine rather than to an associated impurity follows almost certainly from the fact that the *dl*-base is also triboluminescent. The problem of the melting points is still somewhat obscure. On one occasion, the base from *D. canadensis*, when recrystallized from ethyl acetate, was obtained in almost colorless stout prisms meeting at 148-149° C. Subsequent efforts to obtain the base of this melting point have yielded only a product melting at 142° C. The product obtained from dry benzene by addition of petroleum ether melted with effervescence at 124–126° C. and obviously contained benzene of crystallization, which was not lost in a high vacuum over solid potassium hydroxide and paraffin, nor in an oven at 80° C. for 24 hr. The above facts point to the existence of two crystal forms for corydine, although the alternative involving solvent of crystallization is not entirely excluded. In any case, the name eximine is to be deleted from the literature. It is relevant to state here that an attempt will be made to further characterize the author's eximidine when more material becomes available.

The close morphological relation of *D. formosa* to *D. eximia* is thus paralleled by a corresponding identity of some of their alkaloidal constituents. Differences of a quantitative nature are, however, apparent and this becomes more significant when the ratios of the components rather than the absolute amounts are considered. It is therefore of interest that, while *d*-glaucine was found only in traces in *D. eximia*, the ratio to *d*-dicentrine being approximately 100 : 1300, its present isolation from *D. formosa* was in the ratio of 100 : 70 compared to dicentrine. Obviously the process of methylenation is more readily accomplished by *D. eximia*.

A fifth alkaloid was obtained in small amounts. Its phenolic nature and solubility in a variety of solvents, as well as its melting point and color reactions, point to its identity with corytuberine. This appears to be its first isolation from a plant other than *Corydalis tuberosa*.

The investigation of *D. eximia* yielded an alkaloid which was referred to as alkaloid δ. Sufficient of the hydrochloride for analysis has become available and the data calculated for the base are in agreement with the formula $C_{21}H_{25}O_5N$. All attempts to obtain the free base in a crystalline condition

have failed. From *D. formosa* a base was isolated as hydrochloride, the properties of which were in complete agreement with those of alkaloid δ hydrochloride, and for the present the two may be regarded as identical.

Iso-corydine could not be found, although the presence of other bases in extremely minute amounts is suspected.

Finally it was of interest to determine the influence of environment upon the nature of the alkaloid constituents of this plant and for this purpose a small amount of the white flowered variety collected in the State of Oregon, U.S.A., was available. Although the total content of alkaloids was somewhat greater than in the pink flowered variety of British Columbia origin, all the bases found in the typical variety were present and the ratio of glaucine to dicentrine was approximately the same. This observation may be of some interest in that it offers a possible method of confirming botanical classification as applied to species and varieties of species. In this connection it may be noted that an exhaustive comparison of the alkaloids of *D. cucullaria* from two sources, namely, the province of Quebec and Virginia, has failed to disclose any differences other than quantitative, although those from the latter locality are uniformly more robust.

The following experiments were carried out with 11 kilos of dried whole plant material. The results of a smaller scale working with the roots only were not sufficiently different to merit separate description. The total yield of purified alkaloids was 0.40%.

Experimental

In order to obviate repetition the various designations here used have the same significance as in a communication dealing with *Adlumia fungosa* (7). For further simplification and in the interests of clarity the following outline is included:

Base hydrochlorides extracted from aqueous solution by means of chloroform,—

BC—Non-phenolic bases,—Dicentrine, Glaucine.
EC—Phenolic bases extracted from alkaline solution by means of ether,—Corydine.
BCE—Phenolic bases precipitated by carbon dioxide,—Corytuberine.

Base hydrochlorides not extracted from aqueous solution by means of chloroform,—

BS—Non-phenolic bases,—Protopine.
ES—Phenolic bases extracted from alkaline solution by means of ether,—?
BSE—Phenolic bases precipitated by carbon dioxide,—Alkaloid—δ.

Isolation of Dicentrine

The very slight solubility of dicentrine hydrochloride greatly facilitates its isolation from mixtures, and the procedure used for this purpose in the case of *D. eximia* (8) was closely followed. The base mixture (BC), which contained most of the dicentrine and all of the glaucine, was redissolved in dilute hydrochloric acid and the hydrochloride of the former allowed to crystallize as completely as possible. It was observed that a layer of ether on the surface

of the acid solution somewhat hastened this process. The dicentrine (m.p. 169° C.) regenerated from the hydrochloride and the methine prepared therefrom proved to be identical with the corresponding substances previously described (8). Yield of dicentrine: 0.10%.

Isolation of Glaucine

The aqueous mother liquor from which the dicentrine hydrochloride had been obtained was basified with excess potassium hydroxide and the liberated base collected on a glass rod, washed with water, and dried. This was suspended in a large volume of dry ether and disintegrated with a glass rod. The insoluble dark brown powdery mass was filtered off and washed with ether. The combined extract and washings were evaporated to a thin syrup.

This failed to yield any crystalline material during the course of several days. *A priori*, however, it was highly probable that this fraction should contain glaucine, and seeding with a crystal of this base from *D. eximia* induced immediate crystallization. The base was filtered off (m.p. 117–119° C.) and washed cautiously with ether; yield, 0.15%. After one recrystallization from boiling ether it was obtained in brilliant colorless prisms, which alone or admixed with an authentic specimen melted at 120° C. It may be pointed out that glaucine is generally described as being pale yellow, although the impurity responsible for the color does not lower the melting point appreciably. The methine, prepared in the usual way, melted at 75° C. (2, 10).

Isolation of Corydine

The fraction (EC) was dissolved in a small volume of hot dilute hydrochloric acid and the filtered solution (charcoal) allowed to cool. The sparingly soluble hydrochloride which then crystallized was filtered off, redissolved in hot water and the rapidly cooled solution basified with excess ammonia. The precipitated base was extracted with ether and the washed solution rapidly evaporated. Crystallization of the corydine began before all the ether had been removed. After cooling, the base was filtered off and washed with ether. It then melted at 117° C. either alone or admixed with specimens similarly prepared from *D. canadensis* or *D. eximia* (eximine). A specimen recrystallized from purified ethyl acetate melted at 142° C. and when this was admixed with a specimen of authentic corydine from *Corydalis cava* there was no depression of the melting point. Yield, 0.03%.

Another lot was recrystallized by evaporating a clear benzene solution to a small volume and treating this cautiously with hexane. After drying in a high vacuum for 24 hr. it melted with effervescence at 126° C. and had $[\alpha]_D^{25} = +214°$ (c = 1.6 in chloroform) (3).

Still another specimen was racemized by the method of Gadamer (3) and yielded colorless prisms of the inactive base melting at 168° C. All the above specimens exhibited the phenomenon of triboluminescence with great brilliance.

The base was further characterized by O-methylation with potassium hydroxide and nitrosomethyl-urethane in methanol. The non-phenolic fraction was divided into two parts. One portion was treated with an excess of a methanolic solution of *l*-tartaric acid. The *l*-bitartrate of corydine methyl ether, melting with effervescence at 222° C. (4) crystallized almost immediately.

The second portion was neutralized with methanolic hydrogen chloride. The somewhat concentrated solution was treated with dry ether until the incipient turbidity had just disappeared on shaking. In the course of several days the hydrochloride was obtained in fine needles which were recrystallized from a small volume of methanol by the addition of acetone. Corydine methyl ether hydrochloride as thus obtained is anhydrous and sinters at 239° C. and melts with frothing at 250–252° C. Calcd. for $C_{21}H_{25}O_4N.HCl$; C, 64.45; H, 6.63; N, 3.58; OMe, 31.71; Cl, 9.07%. Found: C, 63.86; H, 6.61; N, 3.85; OMe, 30.25; Cl, 9.84%.

A careful search for iso-corydine in the mother liquors from the preparation of the corydine has failed to demonstrate its presence.

Isolation of Corytuberine

This alkaloid was obtained from two fractions, namely (BC) and (BCE), its occurrence in the former being due to occlusion in the bulky precipitate of glaucine. It was recovered from the ether insoluble portion of this (*vide supra*) by dissolving in dilute hydrochloric acid and pouring the solution into aqueous potassium hydroxide. The alkaline filtrate was partly neutralized with hydrochloric acid, then saturated with sodium bicarbonate, and finally with carbon dioxide. The gray granular precipitate was filtered off, washed first with water and then with methanol. Finally it was recrystallized from much boiling water with the aid of charcoal. Colorless brilliant fine needles were thus obtained, which melted at 240–242° C., darkening and sintering taking place at 230–235° C. The fraction (BCE) was washed with methanol and the residue recrystallized from water as above. The combined yield of corytuberine was 0.02%, but owing to the somewhat wasteful procedure employed in isolating it, this figure is undoubtedly much too low. The color reactions with concentrated nitric acid (immediate deep cherry red) and with concentrated sulphuric acid (colorless; after warming, dirty pale green) are those recorded in the literature for corytuberine. Calcd. for $C_{19}H_{21}O_4N$; N, 4.32; 2OMe + NMe, as OMe, 28.34%. Found: N, 4.28; OMe + NMe, 26.06%.

Isolation of Protopine

The isolation and identification of protopine has been repeatedly described in this series of papers so that a repetition is deemed to be superfluous. The fraction (BS) on appropriate treatment readily yielded this base in a pure condition (m.p. 211° C.). Yield, 0.10%.

The mother liquors, however, yielded a small amount of colorless resinous base which could not be induced to crystallize, and so far identification has not been possible.

Isolation of Alkaloid δ

The precipitate (BSE) and the ether extract (EES) were combined, dissolved in methanol, and the somewhat concentrated filtrate neutralized with methanolic hydrogen chloride. Much dry ether was added and the pasty precipitate washed with the same solvent. Addition of a small volume of methanol, and stirring, yielded a sparingly soluble hydrochloride which was filtered off and recrystallized from hot methanol. The colorless fine prisms thus obtained melted with decomposition at 235–237° C. either alone or admixed with a specimen of alkaloid δ hydrochloride from *D. eximia*. Yield, 0.002%. No characteristic derivative has thus far been obtained, so that the question of identity is still an open one. It is to be noted, however, that seeding a supersaturated methanolic solution of the hydrochloride from one source with a crystal from another source induces immediate crystallization, and no property has been observed which would serve to differentiate one from the other. The color reaction in concentrated sulphuric acid is somewhat striking and is reminiscent of that of glaucine. In the cold the solution is colorless, but on gentle warming it becomes greenish blue, which on further heating suddenly changes to an intense and brilliant mauve.

A specimen of the purest hydrochloride obtained from *D. eximia* was dried to constant weight and yielded the following analytical figures. C, 62.31, 61.58, 62.76, 61.80; H, 6.49, 6.56, 6.33, 6.77; N, 3.57, 3.61; OMe, 23.58, 24.09%. Although these figures do not exclude a formula with two hydrogen atoms less, the formula $C_{21}H_{25}O_5N.HCl$ for the hydrochloride is at present preferred. The calculated figures are: C, 61.84; H, 6.38; N, 3.44; 3OMe, 22.92%.

Isolation of Fumaric Acid

The total quantity of fumaric acid was quite small (0.02%) so that it was found only in the ether extract (LC). The residue from the evaporation of the solvent was recrystallized several times from hot water containing a small amount of hydrochloric acid, and the fumaric acid identified by comparison with an authentic specimen (m.p. 287° C. uncorr.).

Acknowledgment

The author takes pleasure in acknowledging his indebtedness to Professor A. H. Hutchinson, of the Department of Botany, University of British Columbia, who arranged for, and supervised the collection of, an adequate supply of authentic *Dicentra formosa*.

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SKRJABINEMA OREAMNI SP. NOV., A NEMATODE PARASITE OF *OREAMNOS AMERICANUS* AND *RANGIFER* SP. IN CANADA[1]

By W. E. Swales[2]

Abstract

An oxyurid nematode of the genus *Skrjabinema* Wereschtschagin, 1926 is recorded from the Columbian mountain goat and mountain caribou in Canada. This parasite is the first Canadian and second North American record for the genus and is described as a new species. A key to the species of *Skrjabinema* is included.

In the autumn of 1933 while studying parasitic diseases of ruminants in Alberta, the writer was enabled to make a study of the helminth parasites of game animals in the Rocky Mountain region adjacent to Jasper National Park. During the course of this investigation, which was carried out through the kindness and co-operation of Mr. S. H. Clark, Game Commissioner of Alberta, specimens of mountain goat or American chamois (*Oreamnos americanus*) and caribou (*Rangifer* sp.) were obtained from the mountainous region surrounding the Little Berland River.

A thorough post-mortem examination was made of the viscera of a young caribou and the only parasites found to be present were numerous female oxyurids which were parasitizing the large colon and caecum.

An aged female Columbian mountain goat also obtained from this region was found upon examination to be harboring many stomach worms as well as numerous oxyurids of both sexes in the large colon and caecum. This material was preserved at the time of collection and a study was made of it following the writer's return to this Institute.

The nematodes from the large intestines were found to be members of the genus *Skrjabinema* Wereschtschagin, 1926. A study of a number of males and females revealed characteristics which appeared to justify the formation of a new species, for which the name *Skrjabinema oreamni* is proposed. The following description is based on the morphological characters of 20 adult males and 20 adult females.

Skrjabinema oreamni sp. nov.

Specific diagnosis. Skrjabinema: Subgenus, *Skrjabinema* Monnig, 1932. Characters of genus and subgenus, although a slightly different interpretation of the lip membranes is given.

The Male

The male is 3.3 to 3.7 mm. long, the average mature male being 3.6 mm. in length; the maximum width is 0.175 to 0.210 mm. in the pre-equatorial

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[2] *Research Assistant.*

region and the body width in the region of the esophageal bulb is 0.121 to 0.138 mm. The head is 0.047 to 0.057 mm. in diameter. The esophagus is typically oxyurid in shape, the length, including the bulb being 0.353 to 0.390 mm. The bulb is subglobular in outline 0.105 to 0.113 mm. long by 0.097 to 0.109 mm. wide.

The mouth opening is surrounded by three small T-shaped lips which are, in turn, surrounded by the wall of the mouth capsule. The lips project inward and somewhat downward. Only four head papillae could be seen in the male. The cervical expansion of the cuticle is narrow and extends to a point a little more than half way from the head to the esophageal bulb. Lateral alae are present and are 10μ wide in the equatorial region of the body and are transversely striated; they extend from the near ring to a point 0.250 mm. from the posterior extremity.

The tail is typical of this genus, being round and blunt, and having a rounded cuticular expansion, 75 to 85μ wide, supported by four lateral processes, one pair pre-anal and the other pair post-anal, each process bearing one papilla at the tip. The two adanal processes, also present, each bear three papillae.

The ventral terminal spike or cuticular fold is 16μ and the dorsal terminal spike is 20μ in length.

The single spicule measures 77 to 85μ, the head being cleft along the median line. The gubernaculum measures 22 to 24μ in length and is closely applied to the spicule throughout its length.

The heavily cuticularized rectum measures 0.173 to 0.192 mm.

The Female

The female is 9.5 to 10.5 mm. in length; the maximum width is from 0.45 to 0.55 mm., at a point approximately 1.0 mm. caudad of the vulva, and from 0.258 to 0.329 mm. wide at the esophageal bulb.

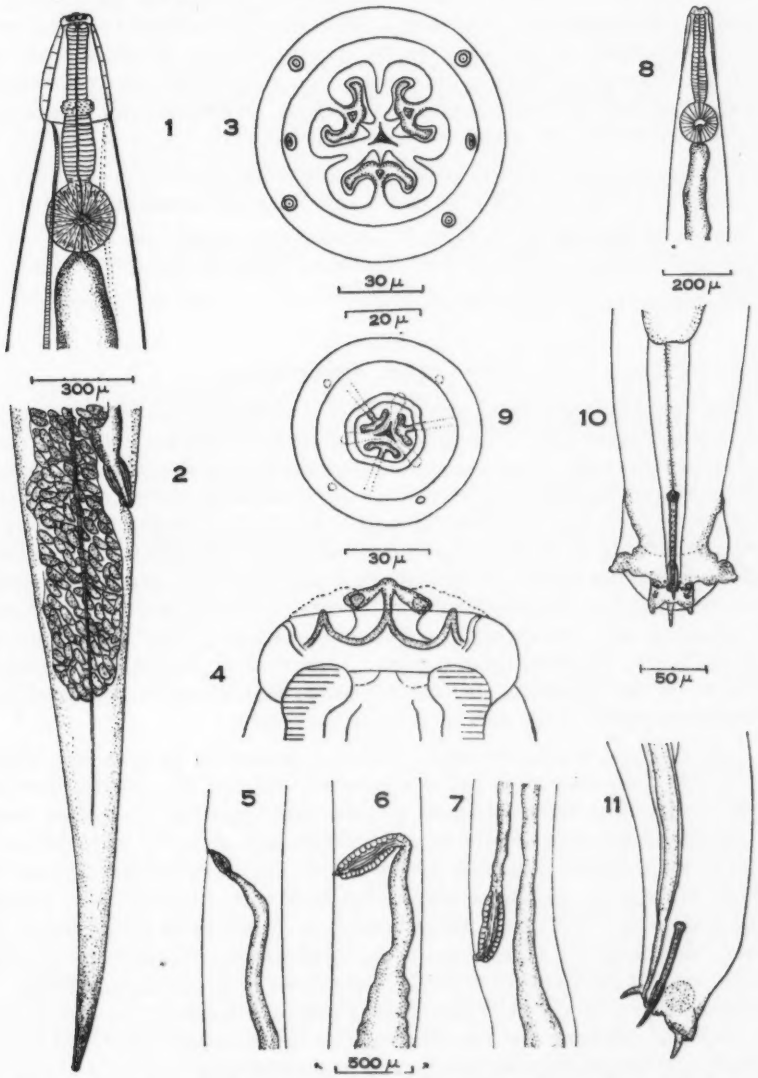
The head is 0.093 mm. in diameter. The mouth opening is surrounded by three anchor-shaped lips, each of which is encased in a cuticular membrane which projects towards the middle line in two lip-shaped structures; these structures have been previously interpreted as separate lips but dissection proves them to be directly attached to the lip membrane.

There are three small interlabia which project into the mouth opening between the lips. Three pairs of papillae are present, these being clearly visible when viewed from the anterior end.

The combined length of the esophagus and bulb is from 0.650 to 0.720 mm. The bulb is globular to subglobular, 0.188 to 0.211 mm. long by 0.196 to 0.219 mm. wide; when globular, as in the majority of specimens examined, it is 0.2036 mm. in diameter.

The nerve ring surrounds the esophagus at a point 0.240 mm. from the anterior extremity. The cervical expansion of the cuticle extends down the esophageal region for a distance of 0.275 to 0.330 mm., the expanded portion

having six coarse transverse striations. The two lateral alae are prominent, and extend from the cervical cuticular expansion to a point less than 0.500 mm. from the caudal extremity.



FIGS. 1-11. *Skrjabinema oreamni* sp. nov. *1. Anterior part of female. 2. Tail of female. 3. Anterior view of mouth structure of female. 4. Dorsal view of head of female. 5-7. Showing vulva and vagina of: 5, immature female; 6, mature female; 7, gravid female. 8. Anterior part of male. 9. Anterior view of mouth structure of male. 10. Tail end of male, ventral view. 11. Tail end of male, lateral view.*

The tail is comparatively long and tapering, being from 1.480 to 1.705 mm. in length, the average of 20 specimens being 1.516 mm. The rectum is cuticularized, 0.120 to 0.150 mm. long.

The vulva is situated at from 2.740 to 3.170 mm. from the anterior extremity, the average distance being 2.981 mm.; it is marked by a transverse slit. The vagina is wide and strong, varying greatly in position and size with the degree of gravidity in the female. In gravid females the uterus extends forward as much as 1 mm. anterad of the vulva. In the majority of specimens examined however, the uterus is entirely caudad of the vulva.

The eggs are typical of the family, one side being flat and the other strongly convex. They are 53 to 57μ in length and 30 to 35μ in width.

The main differences between *S. oreamni* and *S. ovis* are in size. Both males and females are longer and wider than those of *S. ovis*.

The female tail is always much longer.

The Genus *Skrjabinema*

Mönnig (2) lists the known species which at that time were *S. ovis* (Skrjabin, 1915) Wereschtschagin, 1926, from *Ovis aries* in Turkestan and from *Capra hircus* in Turkestan, Austria, the United States and England; *S. tarandi* Skrjabin and Mizkewitsch (5) from *Rangifer tarandus* in north Russia; *S. rupicapra* Bohm and Gebauer (1) from *Rupicapra rupicapra* in Austria; *S. africana* Mönnig (2) from *Rhaphiceros campestris* in South Africa. Mönnig did not find males of either *S. africana* or *S. alata*, but his measurements of the females appear to validate these two species. He proposed two subgenera, *Skrjabinema* and *Chilocrypta*, the former to contain *S. ovis* and *S. tarandi*, and the latter, the other three species. *S. oreamni* sp. nov. will, of course, be included in the subgenus *Skrjabinema* owing to the lips in the female not being surrounded by the wall of the mouth capsule.

Careful comparison of the description of *S. tarandi* by Skrjabin and Mizkewitsch (5) with that of *S. ovis* by Schwartz (4) and Morgan (3) does not reveal any definite difference which is constant between the two species, except in the size of the eggs. Skrjabin and Mizkewitsch show the main difference to lie in the fact that *S. tarandi* has two extra "lip parts" projecting from the middle of each lip, which are not present in *S. ovis;* however, later descriptions show these "lip parts" to be present in *S. ovis* as in all species of the genus. Similarly the differences in the head papillae and expanded cervical cuticle are not apparent when English specimens of *S. ovis* are examined. It is therefore proposed that *Skrjabinema tarandi* be regarded as a synonym of *S. ovis*, thus retaining the five other species in the genus, all of which have definite and apparently constant specific characteristics.

The known distribution of the genus is as follows:—*S. (S) ovis* (syn. *S. tarandi)* in sheep, goats and reindeer, in Turkestan, Austria, N. Russia, U.S.A. and England.

S. (S) oreamni in *Oreamnos americanus* and *Rangifer* sp. in Canada.

S. (C) rupicaprae in *Rupicapra rupicapra*, Austria.

S. (C) africana in *Rhaphiceros campestris*, S. Africa.

S. (C) alata in *Ovis aries*, S. Africa.

PROVISIONAL KEY TO THE SPECIES OF SKRJABINEMA

1. Lips of female not surrounded by wall of mouth capsule and project forward . . . 2
   Lips of female surrounded by wall of mouth capsule and project towards centre of mouth opening 3
2. Tail more than 1.25 mm. in length . . . . . *S. oreamni*
   Tail less than 1.25 mm. in length . . . . . *S. ovis*
3. Distances from head end less than 1.75 mm. and female tail more than .750 mm. long . . . . . *S. alata*
   Head end—vulva 1.75 mm. or more, female tail less than .750 mm. in length . . . 4
4. Head more than 70μ broad, breadth of bulb more than 140μ (immature females only known) . . . . . *S. africana*
   Head less than 70μ broad, bulb less than 140μ in breadth . . . . . *S. rupicaprae*

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STUDIES ON THE BIONOMICS AND CONTROL OF THE BURSATE NEMATODES OF HORSES AND SHEEP

I. THE EFFECT OF URINE ON THE EGGS AND LARVAE IN THE FECES[1]

By Ivan W. Parnell[2]

Abstract

The addition of urine, even when diluted with 25% of water, to both horse and sheep feces, proves to be lethal to the eggs and larvae of all the bursate nematodes in as short a time as 24 hr. Higher dilutions kill a large proportion of eggs and larvae in the same time, and the use of this agent is suggested as being of probable practical value in the control of these parasites.

Introduction

The two large groups into which the nematode parasites of domestic animals fall, are separated by both morphological and biological features. Economically, the more important group is that usually referred to as the Bursate nematodes (on account of the presence of an umbrella-like membrane supported by rays, called the *caudal bursa*, at the posterior end of the males). Members of this group occur in all the domestic mammals but they are specially important in horses and ruminants. In the former hosts, they are further characterized by the presence of a mouth capsule into which the mucosa of the large intestine is sucked and subjected to the action of the worm's digestive juices. This group, which in horses contains several genera and a large number of species, is generally referred to in veterinary literature as the palisade worms or *Sclerostomes*. (The name *Sclerostomum* is an obsolete synonym for the modern *Strongylus;* it is now exclusively used, following the suggestion of Stiles, for the group of worms included in the family Strongylidae found in equines.) The Sclerostomes are widespread in their distribution; practically every equine is infected with them, and undoubtedly they are the greatest single cause of disease to these animals in temperate lands.

Life Cycle

All members of this group have a similar extra-corporal life cycle. The female lays numerous thin-shelled eggs in an early state of segmentation. When passed to the exterior in the feces, these eggs develop further and give rise to a minute larva which, escaping from the shell, feeds actively, probably on bacteria, in the feces. In the course of a few days, this larva (called the first stage larva) moults, and escaping from the cast cuticle, continues to feed and grow. After a second interval, the second stage larva moults, but retains its cast cuticle as a protective sheath. This third stage larva, which is no longer capable of feeding, is the *infective* form and no further change takes place until it is swallowed by the host. It is very resistant to adverse influences, such as variation in temperature, moisture and other conditions.

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[2] *Research Assistant and Honorary Research Associate.*

Control

From the above outline of the free life history, it is obvious that control measures must centre on some method of preventing the larva reaching the infective stage, or of preventing its ingress into the host. The latter involves methods of pasture control, segregation of horses and other considerations. The former involves some method of treating the valuable dung by drying or heating, or by the addition of chemicals. Drying to an extent which will prevent the development of the infective larva or which will kill it once it is reached, is impracticable under farm conditions. It may be employed under military conditions in dry tropical climates, by spreading the feces in a thin layer exposed to the rapid drying action of the sun. Even here however its use is limited.

The use of heat of fermentation has been ingeniously employed by Schwartz who constructed a wooden manure box into which the feces were tightly packed. The heat evolved by the fermentation in the manure destroyed all the larvae in a few days. This method, which involved the use of a special wooden box, is not generally practicable. A somewhat similar result is obtained, however, by building a compact manure heap. The internal part of the heap becomes sufficiently hot but the outer layer does not; it is necessary therefore, to turn in this outer layer every week or so and repack the pile tightly.

The addition of chemicals to the feces has been studied by a number of workers. Nöller and Schmid (8), and Nöller and Korkhaus (7) have carried out some experiments by adding kainit, ammonia salts, lime and phosphates, as well as peat and sawdust to the feces.

Parallel work on the sterilizing of human and canine feces containing eggs and larvae of the related hookworms has involved the use of ammonia salts, lime, caustic soda, salt and urine. These have given some contradictory results, but some of them are promising and suggest the possibility of adding some substance or substances to horse droppings which, while not destroying the value of the manure, would be both economical and practicable.

Experimental

Action of Horse Urine on Eggs and Larvae in Horse Feces

Experiments with Mixtures of Bedding, Urine and Water

In 1933 the writer began an investigation on the possible effect of various kinds of bedding on the eggs and larvae of a mixture of species of Sclerostomes from the horse. As a large number of species are known from this host and as a pure infection with any one form is unknown, no attempt was made to deal with a single species. Throughout these experiments however, feces from animals from the same stable was used in order to make the results comparable; in each particular series feces from the same *animal* was used.

The bedding materials used were straw, sawdust, peat-moss litter and earth. In every case, control experiments without the bedding material

were made. In the first series of experiments, the bedding was mixed with freshly deposited feces in various proportions (see Table I) and placed in quart glass jars, with a loosely fitting lid to permit of aeration. Four pots of each mixture were prepared, two of which were *moistened* with water and two with horse urine. These cultures were incubated for about three weeks (15 to 27 days). To determine the number of larvae which developed, a modification of the well known Baermann technique was employed. The feces was placed in rectangular sieves, which were lowered into warm water (about 35° C.) in battery jars so that the bottom of the sieve rested about an inch from the floor of the jar, and the water just covered the top of the culture. The sieves were left for several days in position, the fluid was then placed in large filter funnels (9-in. diameter) and the larvae collected from the bottom. These two processes were repeated until all the larvae had been recovered. In *no case* were larvae found in the urine cultures. Table I shows the number of larvae found in the water cultures.

TABLE I

EFFECTS OF BEDDING ON WORM EGGS IN FECES

Weight of horse feces, gm.	Weight of bedding	Total larvae obtained	Larvae per gram of feces
60	40 gm. peat moss	2000	33
30	80 gm. peat moss	750	37
40	160 gm. soil	1300	32
40	40 gm. straw	2450	61
100	100 gm. sawdust	6200	62
100	Control	9500	95

From the figures in Table I it will be noted that the largest number of larvae developed from feces unmixed with bedding. When feces was mixed with straw and sawdust about two-thirds of this number developed, and with peat, moss and soil, less than half. While bedding seemed to have some effect on the development of sclerostome larvae, it is obvious that urine had a much more pronounced lethal action. Accordingly further experiments were undertaken to obtain more information on its action.

Further Experiments with Urine, using Modified Technique

The Baermann technique used in these preliminary experiments was clumsy and consumed considerable time; accordingly a more convenient technique was evolved. Material to be tested was enclosed in bags of cheese cloth and suspended directly in the large filter funnels. The samples were repeatedly examined and larvae were counted until only a negligible number remained. The totals referred to below accordingly represent the sum of these various examinations. In some cases, seven or eight examinations were necessary before all the larvae were recovered. Early in the experiments, in order to test whether urine suspensions, because of their greater specific gravity, had prevented larvae from falling to the foot of the funnel, the fluid from the funnels was filtered through filter paper and the paper then washed into small dishes. It was found that the presence of urine had no effect on the rate of recovery of the larvae. The Baermann technique was used throughout all the following experiments.

Feces from the same horse was placed in four quart-jars as before and *covered* with urine in two of the jars and with water in the other two. Small quantities of feces were removed from each jar at the end of three to eight days, and incubated at room temperature, after the removal of the excess fluid. After 14 and 28 days respectively, the fluid was decanted from one jar of each pair and examined for the presence of larvae. The feces was then incubated for several weeks.

No larvae were obtained in either the water or the urine; no worm eggs were found in the urine, but a few were found in the water in an undeveloped condition. From the feces soaked in water (from 3 to 28 days) larvae subsequently developed, but in no case did any develop from feces soaked in urine. A parallel series of experiments using cow's urine instead of horse's, was carried out with identical results. Urine proved lethal to both eggs and larvae, while water proved merely to have a delaying action on the development of the eggs, although prolonged immersion in water appeared to kill some of the eggs.

Effect of Possible Farm Practice

These three series of experiments having shown that urine had a lethal action on the eggs and larvae of horse sclerostomes, a series of cultures were made to test, on a laboratory scale, the effect of possible farm practice, and to determine the concentration of urine and time of exposure necessary to destroy the eggs and larvae.

Fresh horse feces (50 gm.) was used for each culture and mixed with various amounts of horse urine and pure water, only sufficient fluid being used to wet the feces. The feces was examined after 28 days by the modified Baermann technique described above; the results are shown in Table II.

TABLE II

EFFECTS OF VARYING DILUTIONS OF URINE ON WORM EGGS

50 grams of feces moistened with	Larvae obtained
Undiluted horse urine	Nil
Three parts horse urine with one part water	Nil
One part horse urine with one part water	80
One part horse urine with three parts water	2000
Pure water	17600
Not moistened	59000

The Nature of the Action of the Urine

In order to determine whether the fluid had merely delayed the development of the eggs or had actually killed them, the cultures, drained of surplus moisture, were cultivated. It will be appreciated that the large quantity of water used during the Baermann process (which occupied five days) reduced the amount of urine present to a very small amount. After culturing for 12 days, the feces was again examined by the Baermann process. Feces which had been moistened with 100, 75 and 50% urine, produced no larvae. From that moistened with 25% urine, 1650 larvae were obtained and from that moistened with water alone, 2900 were obtained. The unmoistened control produced 1700 in addition to those previously obtained.

TABLE III

RESULTS OF CULTURING FECES AFTER ACTION OF VARYING DILUTIONS OF URINE

Feces moistened with	Larvae obtained
Undiluted urine	Nil
Three parts of urine plus one part water	Nil
One part of urine plus one part water	Nil
One part of urine plus three parts water	4200
Pure water	30000
Unmoistened	28000

A similar series of cultures examined after 38 days produced almost similar results (Table III).

Effect of Time

A series of experiments was undertaken to determine the length of time during which urine has to act on horse feces to prevent the development of infective larvae, and whether stale urine is as effective as fresh. Samples of feces (50 gm.) were again used in each case and the cultures *moistened* with the liquids. To facilitate subsequent handling, the feces was loosely wrapped in muslin bags. Samples were wetted with stale urine (although no free fluid was present in the jars) and after 24, 36, 48, 60, 72 and 96 hr., respectively, were squeezed as dry as possible, moistened with pure water and cultivated for about a fortnight at room temperature. They were then examined as before for the presence of larvae. In *no case* were larvae found. Samples similarly moistened with fresh urine for 36 and 60 hr. respectively were also negative, while control samples treated with water produced 5200, 800, 240 and 2200 larvae respectively after 24, 48, 72 and 96 hr. respectively.

Similar experiments with cow's urine showed that its effect was identical with that of horse urine.

Effect on Larvae at Various Stages of Development

To ascertain the stage in development at which urine is most lethal, another series of cultures was made. Fresh feces in four sets of jars, each containing 50 gm., was cultivated for one, two, three and four days respectively and then soaked for 24 hr. in horse urine; the fluid was then decanted and the feces thoroughly mixed with about 10 times its volume of water. Little, if any urine could have been left in the feces which was squeezed dry, moistened slightly with water, and cultivated for about a fortnight. The wash water was filtered and the filtrate was also similarly cultured to recover any eggs or larvae which might have otherwise been lost during washing. In none of these cases did larvae develop.

Two sets of feces were soaked in urine for 24 and 48 hr. respectively; the urine was then squeezed out and the feces was cultivated as before (after washing) for a fortnight, and examined for larvae. In the first case, 140 larvae were recovered, while in the second the culture was negative. In controls similarly treated with water instead of urine, 25,000 and 15,000 larvae respectively developed. As there was no surplus urine in these cultures, it is possible that a small area on the top escaped the action of the urine and that this accounts for the 140 larvae, rather than the fact that the action of the urine was only partly lethal.

Simultaneously with the previous experiments, feces from the same horse was cultivated in 50-gm. lots for a fortnight. One lot was then soaked in urine for 24 hr. and a second for 48 hr. and both feces and urine examined for the presence of larvae. In the case of the sample soaked for 24 hr. in urine, 15,000 larvae, and in that soaked for 48 hr., 2200 larvae, were obtained. In both cases all the larvae were dead. In the controls, treated in an identical manner, but with the substitution of pure water for urine, 65,000 and 50,600 active, living larvae respectively were obtained.

These experiments show that urine of the horse and the cow has a lethal effect on both the eggs and larvae of the horse Sclerostomes in manure, while water has merely a delaying action on the development of the eggs, although a portion of the eggs are destroyed on prolonged immersion in water. Undiluted urine as well as urine diluted with 25% of pure water kills all the eggs and larvae, but a large proportion is destroyed by as low a concentration as 25% of urine in water, in as short a time as 24 hr.

Action of Urine on Eggs and Larvae in Sheep Feces

A related group of worms is one of the commonest sources of loss among sheep, and the opportunity was taken of the presence of heavily infested sheep at the Institute to test the effect of urine on the eggs and larvae present in their feces. Samples cultivated for 30 days after being treated with concentrated urine or urine diluted with 25% of water were free of larvae, but a large number of larvae developed when solutions of lower concentrations were used. It was interesting to note that more larvae developed from unmoistened feces than from feces moistened with pure water. A second series of experiments, identically treated but cultured for 37 instead of 30 days, yielded no larvae from samples treated with concentrated, 75, 50 or 25% urine. The controls again gave a heavy culture.

To ascertain whether urine had been lethal to eggs in sheep feces or early stage larvae and had not merely delayed development, the second series of sheep feces was recultivated for 12 days, it being again assumed that since the wash water was many times the volume of the highest concentration of urine, at least some larvae would develop if they had not been killed by the urine. A number of larvae developed only from the 25% dilution of urine. As this number was only about $\frac{1}{15}$ of that obtained in the controls, it may be assumed that even the weakest dilution was partly lethal to the eggs and wholly so to the larvae.

Conclusion

Urine accordingly appears to be a possible agent which could be used in the practical control of bursate nematodes in horses and in stabled sheep. Not only is it available simultaneously with the feces, but it costs nothing beyond the cost of collection and it not only does not lessen the manurial value of the dung but actually increases it.

Experiments are at present in progress at the Institute of Parasitology to ascertain the most economical and practical method of using urine under actual farm conditions as a method of controlling what is now the most serious and widespread cause of disease in horses, and which is found in all civilized countries.

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COLOR CHANGES IN SNOWSHOE HARES[1]

By S. Hadwen[2]

Abstract

Observations on the color changes in *Lepus americanus virginianus* in Ontario are recorded. The production of pigment may be influenced by the fact that the hares can have more than one litter per season. The skin is thicker in the unprime condition than in the prime. From a study of melanin formation in the hair roots it was found that there are produced in succession several kinds of pigments which form the color pattern in the full grown hair. The structure, percentages, and types of hair are discussed. Kempy fibres are recorded. A different type of hair on the soles of the feet is described. This hair apparently grows independently of the hair on other parts of the body. Reasons are given for the erectness of winter fur as opposed to flat lying young summer fur. Hares were clipped on one side of the body. In two cases the regrowth of fur produced bands of color and then whitened above; the hairs were identified by the cut ends. Dyeing experiments showed that when brown hair whitened it lost part of its own natural pigment and the dye as well. In two cases where the tips of the hairs had been cut, the dye ran inside and permanently marked them.

Introduction

The nature of the color changes that take place in the fur of northern hares has long been an unsolved problem. The experiments described here were planned to show what alterations actually occurred in the skin and hair of living animals. The two main objects of the investigation were (i) to prove that the blanching of the fur of snowshoe hares is caused by a process of depigmentation and masking of pigment in the hairs, and (ii) to confirm the writer's previous observations (10). The observations were made in Ontario on *Lepus americanus virginianus*, which lives in the northern part of the province. A previous paper (10) dealt with the Manitoba snowshoe hare, which differs a little from the Ontario form, but has the same habit of turning white in winter; therefore, in relation to the pigmentary changes, the two subspecies may be regarded as similar. Two methods were tried, *i.e.*, clipping the fur, and dyeing it before it turned white.

That the whitened fur still contained pigment was proved by microscopic examination. The disappearance of melanin had to be shown by experiment. In general it may be stated that the observations confirm the results obtained by the writer (10) in 1929. All photographs in this article are from untouched negatives.

Experimental Animals

General Remarks

The experiments began in November 1932 and continued up to 1934. About 50 hares were either captured alive or shot, and 20 were caged for varying periods. Five hares were alive at the conclusion of the work. Eight captured hares were caged from May 1933 to the close of the year.

[1] *Manuscript received March 19, 1934.*
Contribution from the laboratories of the Ontario Research Foundation, Toronto, Ontario, Canada.

[2] *Director of Veterinary Science, Ontario Research Foundation.*

Table I gives a general idea of the coloring of the animals at different periods. The first change noted was the whitening of the ears and feet, which began as early as September 6. The more striking changes which start later, such as blanching of the face, usually take about 30 days (average of 10 animals) but they may take longer—up to 60 days or more. The first of the caged hares to become white did so on November 1, and the last about January 10.

Starting in April when the white portion of the fur was shed the hares turned brown, except for a little white which remained on the face, ears and feet. In May and June the backs of the ears became devoid of hair. On June 23, out of eight newly caught hares, four had white skins and four dark. The white-skinned hares had the normal summer coat and their ears were furred. The dark-skinned animals had poorly furred ears and the darkness of their skins showed that the hair had not finished growing. From July onward there was no noticeable moult in any of the caged hares, except in one instance, No. 23. This animal had a short woolly coat up to September 26.

Among the hares which were shot during the summer several moulting specimens were secured. It will be noticed in Table I that a thin white prime skin was recorded as early as May 12, but most of the white skins were collected from July onward. As the prime condition of the skin means that the hair has ceased growing and must be replaced later by new hair, these observations should be continued in order to determine exactly how long it takes for the animals to grow a new coat of fur, and whether this may be accomplished more than once during the summer. This point is discussed later in connection with the experimental clipping. Two hares, No. 34 and one which is still alive, did not whiten completely. No. 34 had a small patch of brown on the forehead on January 10. One of the captured hares (No. 32) died of pneumonia. This animal had an abnormal coat. There were a large number of short degenerating white hairs near the skin. These hairs had whitened before they had completed their growth and it is possible that they ceased growing when the hare became ill. This is the only abnormal coat found in the series.

The caged hares were kept in separate pens and consequently had no chance to mate. The animals were housed in a steam-heated room and at no time were subjected to cold. A caged hare began to shed its white coat on February 20, another on March 9. Large numbers of guard and pile hairs with roots attached were found on the bottom of the cages.

Number of Litters

As the bearing of young may have an effect on the coat, it must be taken into consideration, and therefore the breeding habits of the hares were noted whenever possible. It would appear that Ontario hares may have one or more litters per year. This is based on the fact that pregnant "does" were shot at different dates during the spring and summer. On July 25 at Geneva Lake a doe that was milking was shot and found to have four small fetuses

TABLE I

CHANGES IN SKIN AND HAIR OF RABBITS

Skin No.	Date received	Received from	Appearance of hair	Appearance of skin	Microscopic appearance
	1933				
1	Jan. 15	Cartier, Ont.	White	White and thin	Root ends frayed
2	Jan. 15	Cartier, Ont.	White	White and thin	Root ends frayed
3	April 12	Cartier, Ont.	White, soles of feet blue	Slight spotting	Root ends frayed. New pigmented roots
4	April 17	Cartier, Ont.	White, soles of feet blue	Spotted brown and black with new growth below the hair	Root ends frayed. New roots red and black
5	April 23	Cartier, Ont.	Mostly brown	Very dark and blotchy	Pigmented roots
6	April 25	Cartier, Ont.	Ears white and brown	White with slight spotting	Frayed roots and pigmented roots
7	April 26	Kirkfield, Ont.	Almost brown on back. A few patches of white. Soles of feet blue	Darkish line along skin of back	New roots red and black
8	April 26	Kirkfield, Ont.	White. Ears white	Very black	Pigmented roots
9	April 27	Cartier, Ont.	Brown and white	Dark brown and black	Pigmented roots
10	April 29	Cartier, Ont.	Mostly brown. Ears brownish, feet blue	Spotted	Frayed roots and pigmented roots
11	April 29	Cartier, Ont.	White. Ears white. Feet blue	Black and brown	Pigmented roots
12	May 1	Cartier, Ont.	Brown and white. Ears white	Blotchy	Pigmented roots
13	May 2	Cartier, Ont.	Brown and white. Feet blue	Very dark	New roots pigmented
14	May 12	Cartier, Ont.	Hair brown. Back of ears bare; soles of feet blue	Nearly white and few spots present	Frayed roots and pigmented roots
15	July 25	Geneva Lake, Ont.	Very dark; back of ears bare	Thin with few black spots	Skin white; no black roots
16	July 25	Geneva Lake, Ont.	Short. Ears bare, feet brown, soles dark	Mottled black	Hair roots degenerated; only small ones left
17	July 25	Geneva Lake, Ont.	Fur dark and new looking. Ears naked at back. Feet brown with few white hairs. Soles dark colored	Whitish; few black spots	New roots growing black and brown
18	July 27	Geneva Lake, Ont.	Brown. Ears partly bare	Thin and white	Roots frayed
19	Aug. 2	Geneva Lake, Ont.	Fur loose on back. Ears naked; feet brown; soles dark	Almost black	Large roots becoming pigmented; small roots black; no new brown roots. A few large roots growing on side
20	Aug. 2	Geneva Lake, Ont.	Hair shedding. Backs of ears naked. Feet brown; soles dark. Still a few white hairs attached (winter?)	Whitish except for few spots	Return of pigment brown and black in spots
21	Sept. 17	Cartier, Ont.	Ears and feet brown. Soles of feet dark. Hair brown and erect	Bluish	Last traces of pigment in roots. Outlines of roots in melanin (?)
22	Sept. 25	Cartier, Ont.	Erect; ears whitish; feet brownish; soles whitish	Thin; very slight spotting	A few fine hair roots with degenerative pigment
23	Sept. 26 (caged)	Cartier, Ont.	Scanty yellow hair matted and old. Ears and feet whitish. Soles white. Above yellow line regular brown fur	Dark except yellow line along back, where it was thick	On line in centre of back, new brown and black hair roots; on dark parts of skin only black roots; yellow area more vascular than black

TABLE I—*Concluded*

CHANGES IN SKIN AND HAIR OF RABBITS

Skin No.	Date received	Received from	Appearance of hair	Appearance of skin	Microscopic appearance
	1933				
24	Oct. 6	Cartier, Ont.	Erect and brown. Whitish feet and ears; soles whitish	Thin and whitish	No pigment in hair roots; ends frayed
25	Oct. 10	Cartier, Ont.	Brown and erect. White ears and feet	Thin and whitish	No pigment in roots; ends frayed
26	Oct. 18	Cartier, Ont.	Nearly white	Thin and nearly white	All roots frayed at ends
27	Oct. 18 (caged)	Cartier, Ont.	White and erect. A few black spots on flank. No growth on clipped side on feet and ear	Thin and white	A few pigmented hair roots on clipped side; ends frayed
28	Oct. 18 (caged)	Cartier, Ont.	Erect. Soles of feet whitish	Whitish except line along back	A few small roots with degenerated pigment on line along back
29	Oct. 19 (caged)	Cartier, Ont.	Unclipped side normal brown. Brown and fawn on clipped side. Feet brownish; soles white. Clipped ear and feet no growth	Yellow line on back. Rest of skin blackish	Only small hairs with black pigment. Large roots degenerated
30	Oct. 19 (caged)	Cartier, Ont.	Erect and nearly white. Feet whitish; soles white	Thin and whitish. Black along back of head	Only small roots with degenerated pigment
31	Oct. 19 (caged)	Cartier, Ont.	Dark. Fawn on clipped part	Dark and thick	Hair roots degenerating
32	Oct. 23–Nov. 1	Cartier, Ont.	Brown	Very thin and white	A very few pigmented small hair roots; other roots frayed at ends
	1934				
33	Jan. 9	Cartier, Ont.	White	Very thin and white	All roots frayed at ends
34	Jan. 10	Cartier, Ont.	White	Thin and white	All roots frayed at ends
35	Jan. 15	Cartier, Ont.	White	Thin and white	Roots frayed at ends. A few very small black spots with active roots
36	Jan. 18	Cartier, Ont.	White	Thin and white	Roots frayed at ends. A few very small black spots with active roots

about two weeks old. Additional data obtained concerning litters and fetuses are as follows. On April 26, two fetuses were found in a doe, and on May 4, six were found in another. On May 19, two young were born to doe No. 7; on May 21, one to doe No. 5; and on May 22, three to doe No. 6. On July 23, four fetuses were found in a doe; and on July 25, three, two, and four fetuses were collected in different "does".

Mr. Stewart Criddle of Manitoba informs the writer that snowshoe hares in that province have two, or possibly three, litters per season.

Grange (7) states, "One captive female produced two litters during the same summer. Whether or not this occurs in a state of nature we do not know."

The Skin

Pigmentation

The pigmentation of the skin, with the exception of the exposed parts such as the eyelids, is due to the pigmented hair roots which show through the colorless epidermis. In the spring, black patches appear in the region of the tail head. These spread out over the body, extending rather irregularly downward over the flanks. In autumn, the reverse process occurs, that of whitening, starting from the feet and extending upwards. The last portion to lose its pigment is a line over the backbone. Primeness of the skin occurs both in summer and winter. But there is a difference in the primeness in these seasons; in winter when the hair is white the skin is always prime, whereas in summer when the fur is brown the skin may be prime or unprime according to the growing condition of the hair.

Measurements

The skin of hares varies in thickness at different seasons, and these variations are intimately connected with the growth or death of the hair roots. The period of growth is accompanied by increased vascularity, glandular activity and thickening.

Through the co-operation of Mr. Henry of this Foundation, 17 skins were measured, and though this is perhaps too small a number to serve as a basis for a definite statement, nevertheless there was a distinct difference in thickness between prime and unprime skins.

Primeness in the Skin of Other Animals

Blanching of the skin occurs in animals such as the muskrat, which, unlike snowshoe hares, do not whiten. The blanching stops just above the hair roots. This difference has been interpreted as showing that the process in hares is not a destructive depigmentation. This, however, does not appear to be correct as once a hair root has become frayed at the end it is dead and cannot return to an active state of pigment formation.

On examining the ears of hares which had turned white, it was found by the writer that on the edges and also at the tip where the hair remains colored, the roots whiten and become frayed at the ends, just as they do in the muskrat, and though the areas in which this occurs are small they show the same type of depigmentation of the roots without extension up the hairs.

The Hair Roots and Pigment Formation

Fig. 5, Plate I, shows the egg-shaped hair bulb with a clear space at the end. Surrounding the hair as it emerges from the bulb is a well marked sheath which continues up above the root. It must vary considerably in diameter owing to the uneven width of the hairs. Blood vessels surround the bulb and may be seen in Fig. 6, Plate I. No arrector pili muscles have been demonstrated though they have been mentioned by other writers.

The formation of melanin is entirely confined to the root. When the hair roots begin to grow, melanoblasts collect in small groups, and if they are

examined in a clear area of the skin no other cells appear to accompany them (Plate I, Fig. 8). As the cells reproduce, the tip of the new hair is formed. A noticeable feature in the new hair tips is presented by the spiral twists which remain at the ends of the fully grown hairs. The twists occur in clear transparent areas where there is seemingly no resistance offered to the advancing tip, except that due to the fibres of the skin itself. It has been suggested that spirals are due to the moulding effect of the epidermal cells, but this is evidently not the case, the spirals being formed early in the growth of the roots (Fig. 1). The root then becomes more clearly defined though the sheath is not formed until the hair has grown longer. At this stage there is a sudden alteration in the character of the pigment in the roots from black to a fine reddish brown. After a further period of growth the brown melanin changes again to slightly coarser dark brown pigment. The last stage of pigment production in the root is the longest and represents a growth of hair of 1–1½ cm. and the pigment is made up of coarse oval-shaped grains. All the stages mentioned may be seen in the figures in Plate I. The hair roots in similar stages have a uniform appearance, but pigment formation does not proceed evenly in all the roots at the same time, as they are in different stages of growth, although the precursors of melanin formation must be present in all parts of the skin (Plate I).

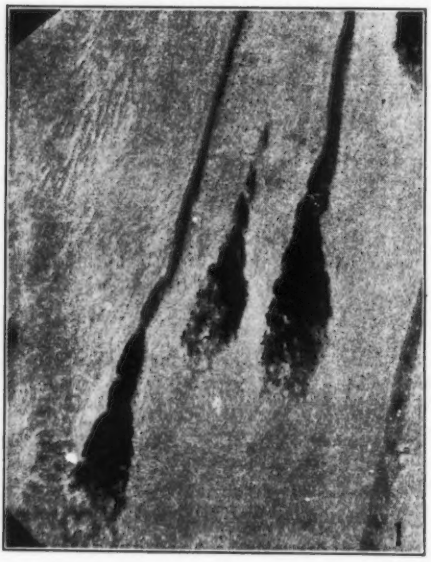


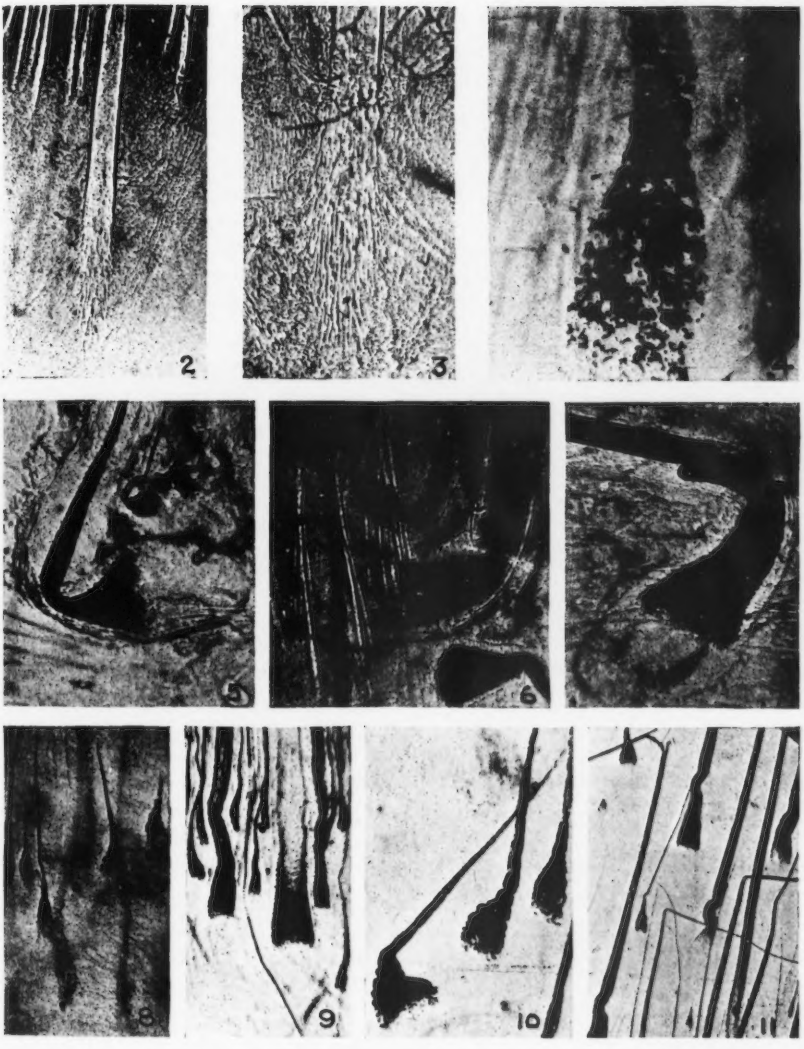
FIG. 1. *The young hair root in the centre shows the individual cells pointing in different directions, forming a spiral. In the roots on either side the process has gone further.*

The Fur

General Description

In summer the fur is banded as follows: from the skin outward the colors are blue-black, fulvous, dark brown, light yellow and black. In winter it is bluish-black, fulvous, dark brown and white. The summer pelage corresponds with the colors produced in the hair roots. The same general banding may be seen in the fur of other animals, such as deer and squirrels.

The principal difference between the summer and the winter coat is confined to the guard hairs and the pile, which whiten after the skin becomes prime. These winter hairs not only whiten at the tips but, in the case of the guard hairs, they have a whitish appearance right down to the skin. The word whitish is used because these hairs are actually of a bluish color



FIGS. 2-3. *Straight roots in prime winter skin. Note broken bits of tissue above frayed roots.* FIG. 4. *Hair root losing its pigment.* FIG. 5. *Hair root showing sheath. (About 230 diam.)* FIG. 6. *Root with encircling blood vessels; producing rusty pigment. (About 230 diam.)* FIG. 7. *Root producing black pigment. Note kink above. (About 230 diam.)* FIG. 8. *New hairs. The faintly colored roots were once black but now are producing rusty pigment; later they will produce black pigment, as in Fig. 9.* FIG. 9. *Change in pigment production from red to black.* FIG. 10. *Young hairs, bulbs forming. (High power.)* FIG. 11. *Hairs bent at point of exit through the skin. (Low power.)*

when pulled out and examined over a piece of white paper. They constitute a small percentage only of the white coat (16–25%) and are not numerous enough to whiten or obliterate the colored bands below. The pile hairs which constitute 75–85% of the white fur have an attenuate base so that they become invisible in the colored bands (Fig. 28).

The undercoat of snowshoe hares does not bleach. This is the reason why the bands remain after the outer coat has changed color. In the larger hare, *L. campestris*, the undercoat whitens almost completely on most parts of the body.

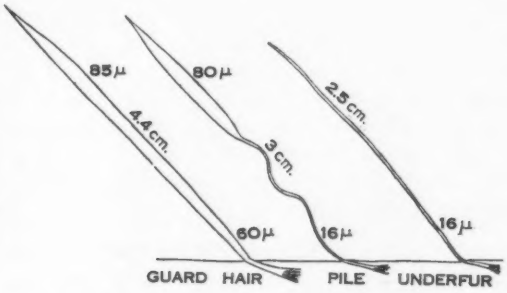


FIG. 28. *Illustrating three main types of hairs.*

It should be mentioned that there are present a certain number of hairs which are intermediate between guard hairs and pile, but not in sufficient numbers to materially alter the percentages given.

Percentages of Guard and Pile Hairs

The percentages of guard and pile hairs were estimated by the writer by mounting small locks of hair on slides and counting the number of large hairs which reached the skin end of the lock. This gives the number of guard hairs. The slide was then moved forward and the number of wide hairs counted at the free end. This gave the total number of guard and pile hairs. From these figures the percentages of each could be calculated.

Measurements of Hairs

Data obtained on the measurements of hairs are shown in Table II. The

TABLE II

MEASUREMENTS OF HAIRS

—	Summer fur	Winter fur	—	Summer fur	Winter fur
Blue-black	1.3 cm.	1.5 cm.	Width of guard hairs:		
Fulvous	0.5 cm.	0.5 cm.	Outer end	84.8μ	85.0μ
Dark brown	0.5 cm.	0.5 cm.	At skin	60μ	60μ
Light yellow	0.5 cm.	No longer present	Outer coat	25%	16%
Black	1.0 cm.	Only slight amount at tip	Width of pile hairs:		
			Outer end	78.0μ	80.0μ
White	—	2.5 cm.	At skin	16.0μ	16.0μ
Length of guard hairs	3.8 cm.	4.4 cm.	Outer coat	75%	84%
Length of pile hairs	3.0 cm.*	3–3.5 cm.*	Under-fur	2.5 cm.	2.5 cm.

NOTE:—*See Figs. 12, 13, 14 and 15.* **Approximately.*

total length of the summer fur, taken shortly before the change to white, is 3.8 cm. The winter coat is 0.6 cm. longer. There is not as much difference in length, as many believe, between the full grown erect summer hair and the winter fur, as the latter is white, giving the impression of greater length.

The measurements show the width of the hairs in the pigmented zones. The width of the hairs affects the coloration of the bands both in winter and summer, and the percentage of the different types of hairs also contributes to the banded coloration of the fur. To avoid confusion an explanation as to the exact meaning of white, as applied to hair, is necessary. Strictly defined, a white hair is one which contains no pigment. But the bleached or whitened hair of the snowshoe hare contains a little pigment at the tip and a considerable amount at the base, which means that it is not pure white like albino hair; the white effect, then, is due to reflecting surfaces which obscure the underlying pigment.

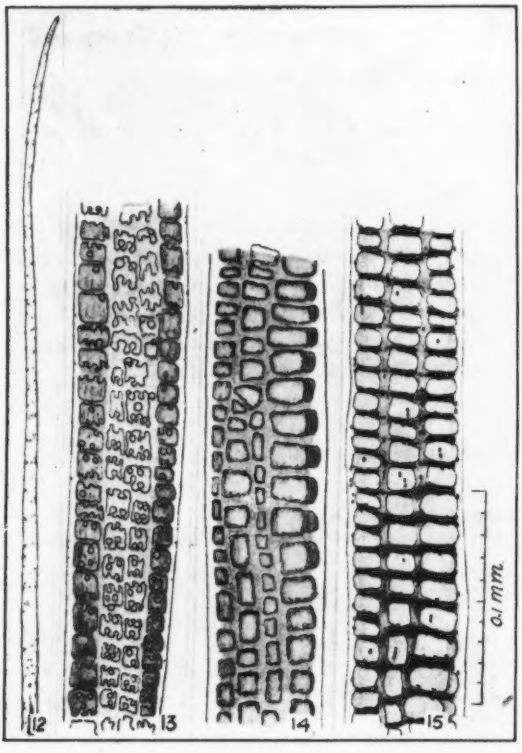


FIG. 12. *Tip of guard hair showing pigment and spiral turns.* FIG. 13. *Wide portion of hair with air bubbles and degenerate cells. This was formerly the yellow zone.* FIG. 14. *Zone in which pigment has disappeared. The cells are widely separated.* FIG. 15. *Blue-black zone near skin. (Drawn by A. M. Fallis.)*

Summer Fur (Microscopic Appearance)

The guard hairs in the summer fur are stiff supporting hairs, as the name indicates. From the tip, which is coal black and shiny (9 μ in width), down, the hair widens rapidly and the black pigment fades out as it reaches the yellow zone where the hair is widest (see Figs. 12–15, which are drawn to scale). Here the cuticular strip shows as a shiny wide transparent zone surrounding the hair. The shiny cuticle has the same effect as shellac over patent leather, enhancing the yellow color. It is in this yellow area that air bubbles are numerous both inside and outside the hair cells (Plate III, Fig. 23). Farther along the hair, the cuticular strip narrows down, owing partly to the presence of small dark

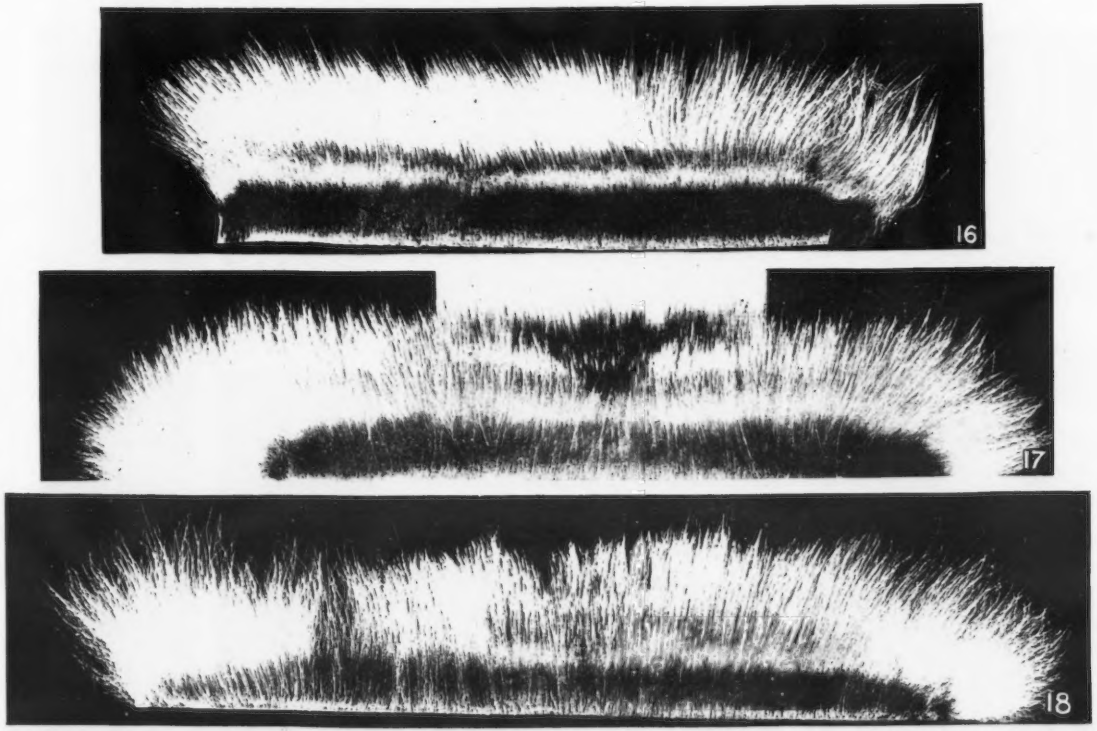


FIG. 16. *Prime winter fur.* FIG. 17. *Changing fur. The dark brown portion at the centre is turning white and is isolated from the rest of the coat. This furnishes evidence of the change of color in existing fur.* FIG. 18. *Section through the fur of Hare 30. Clipped and dyed with Aniline blue. The color bands are irregular on left side. Note cut ends of hair. Re-grown hair not as long as on unclipped side.*

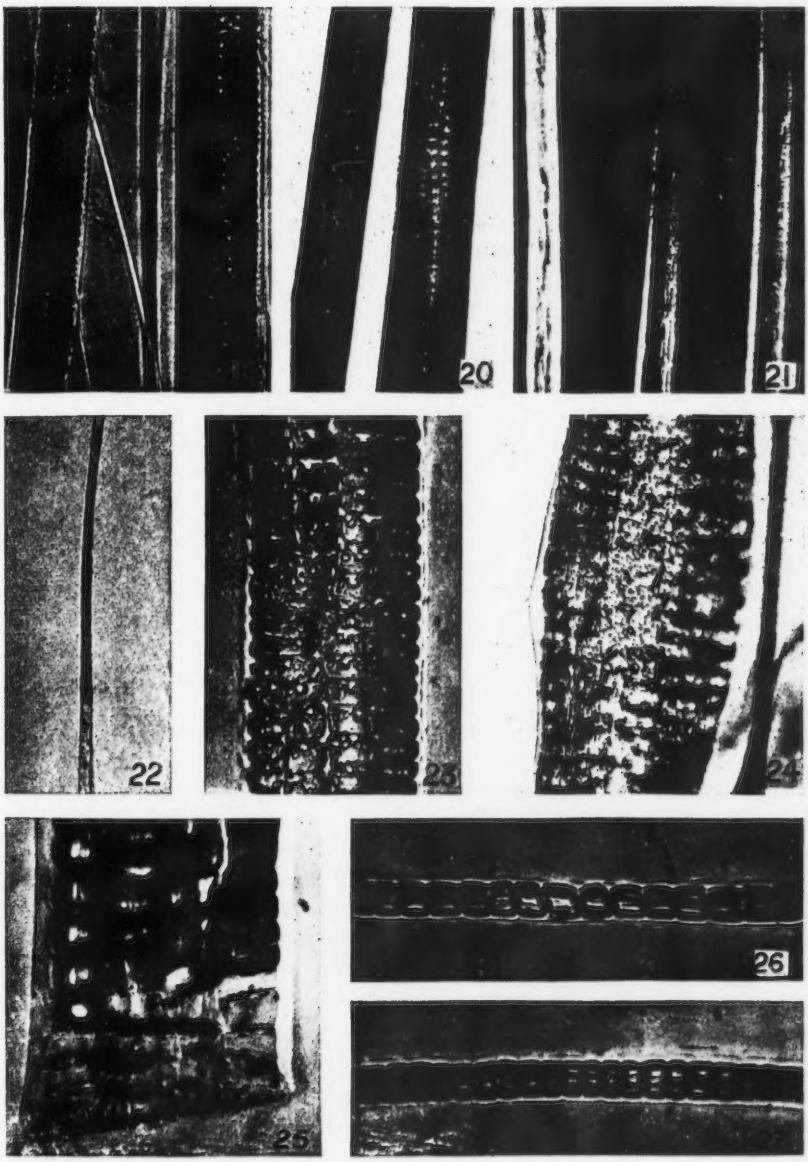


FIG. 19. *White albino hair; domestic rabbit. (About 160 diam.)* FIG. 20. *Black hair; domestic rabbit. (About 160 diam.)* FIG. 21. *Black and white hairs; snowshoe hare.* FIG. 22. *Tip of whitened hair still containing pigment. (About 360 diam.)* FIG. 23. *Air bubbles inside and out of hair cells. (About 360 diam.)* FIG. 24. *Finer type of pigment which disappears. (About 360 diam.)* FIG. 25. *Whitened guard hair with pigment grains. (About 360 diam.)* FIG. 26. *Base of pile hair near the skin.* FIG. 27. *This is the same hair as in* FIG. 26 *but closer to the skin. Note spaces between cells tightly packed with melanin.*

brown grains of melanin which take up space and give the hair a dark coloration. Below this area the hairs often show irregularities in width but broaden out again, and from here down to the skin become heavily banded with large oval-shaped grains of melanin. The grains of pigment lie close to the hair cells producing the blue-black coloration (Fig. 25, Plate III).

In 1929 the writer (10) showed that the attenuate base of the pile hairs breaks off readily when the hair is pulled, and an experimental hare was plucked in the white state. In examining moulted hairs on the bottom of the cages in 1934, he found that, when naturally shed, both pile and guard hairs have their roots attached. It would therefore appear that many of the hairs are shed intact and that it is not necessary for them to break off above the root at moulting time.

Winter Color of Hairs

The winter and summer hairs differ but little, except as regards color and length. The guard hairs are about a centimetre longer in winter and the other types of hairs lengthened in proportion. The whitening of the guard and pile hairs is due to two principal causes, the first being a degeneration and shrinking of the fibres and the second a disappearance of melanin.

Both guard hairs and pile become twisted and flattened. The centre collapses and the sides of the hairs become rounded. The cuticle becomes very shiny and glassy, and has a mirror-like effect. The cells in the hairs shrink and degenerate so that light passes between them. This effect and that of the shiny cortical strip produce the effect of whiteness. The finer types of pigment, the yellow and the fine dark brown, are the ones that disappear. At the tip of the hair, following the spiral twists, a small amount of black pigment remains. This pigment and the coarse black pigment at the base appear to be much more resistant to change than the finer types of melanin.

It has been stated that the production of pigment in all the roots does not occur simultaneously, and the same thing applies to the whitening hairs which do not all become white at once but only in certain areas at a time For instance, the guard hairs whiten a little in advance of the pile and, being longer, are plainly visible over the dark under-fur.*

Air Bubbles in the Hair

Air bubbles in the hairs are mentioned by a number of writers. Welsh (16), Poulton (13) and Verne (15) believe that the white color of the hair is due to air bubbles. The writer mentioned air bubbles in 1929, and at that time he thought that they contributed to the white coloration. Since then he has found that bubbles occur in colored hairs; therefore it cannot be said that they cause the white coloration.

**The disappearance of melanin in the hairs may be very clearly seen in the long vibrissae on the face. These hairs have a horsehair type of conformation. White patches appear, often, about the middle of the bristle. The cortical part becomes white and transparent and the fine granular pigment fades away. In the snowshoe hares the vibrissae whiten about the same time as the fur.*

Nevertheless, through their reflecting surfaces in conjunction with the hyaline cortical strip, bubbles may enhance the white effect.

Kempy Fibres

Kempy fibres are frequently observed in snowshoe hares. These fibres differ from the hairs in the whitened coat, inasmuch as the degeneration has gone much further. The outlines are distorted and the hairs consist of little else than the shell of the former hair (Plate IV, Fig. 29).

In the regrowth of fur which followed the clipping of three of the experimental hares, Nos. 4, 5 and 7, there were many of these fibres, not only of guard hairs and pile but of the underfur likewise.

It should be mentioned that these kempy hairs grew up from the clipped hair roots. After the hair had grown long and had turned white the hairs could be identified by their cut ends. In many of the hairs the kempiness did not extend all the way down to the skin, and it may be that the degeneration started from the cut end.

White Star on Forehead

This is commonly present. Mr. D. A. MacLulich gave the writer figures for 22 hares, of which 12 showed definite white spots. Of 12 animals examined the writer found 9 with stars. It would seem that the white star is an inherited character at the line of union on the forehead and is present in about 75% of the animals. The hair growing on the star is comparable to that on either side of the linea alba, which is albinotic also.

The Hair Cover of the Under Surface of the Feet

Five hares were clipped over one half of the body including both feet and one ear. This was done after the outer covering of the feet and ears had whitened. No growth of fur occurred on the upper surfaces of the feet and ears. This was to be expected, because when the fur is white the skin also is white and the hair roots are dead. But, peculiarly, a new growth occurred on the soles of the feet. This clearly showed that there was something different in its character, and that it grew independently of the hair on the rest of the body.

As an experiment, a hare's foot was dipped in basic fuchsin. The dye instantly colored the hair on the plantar surface a bright magenta, whereas it dyed the upper parts only lightly. Under the microscope it was observed that near the skin the hairs were medullated with a very wide cortical strip, and that farther out they were twisted spirally. Probably through wear, the cortical strip in the spiral portion becomes fringed so that it has almost the appearance of a feather. This explains why the dye colored the hairs so deeply; the deep coloration was due to the penetration of the dye into the fringe. The above also explains why the soles of the feet are differently colored at various times of the year. In the spring they are noticeably blue-black. Dr. R. M. Anderson of Ottawa showed the writer some hares' feet, of which the under surface was a canary yellow (Plate IV, Figs. 30 and 31).

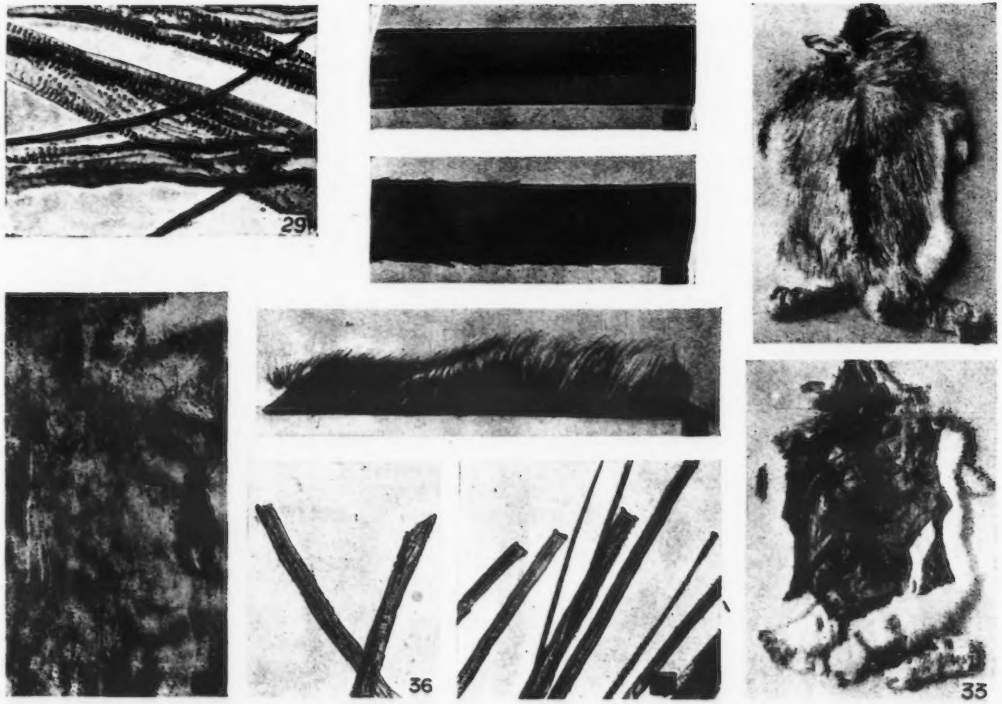


FIG. 29. *Kempy fur. Twisted distorted fibres.* FIG. 30. *Hair from sole of foot. Note wide cortical strip.* FIG. 31. *Hair from sole of foot. Outer portion. Note fringe which is produced by wear.* FIG. 32. *Note dark line in fur—the last part to whiten.* FIG. 33. *Underside of skin seen in Fig. 32. This shows that the pigment in the hair roots coincides with hair color.* FIG. 34. *Skin cut lengthwise along back, showing erectness of light fur compared with that of the dark fur.* FIG. 35. *Unprime spots in skin.* FIG. 36. *Hairs from hare No. 30, tipped with Aniline blue.* FIG. 37. *Red tipped dyed hairs from hare No. 34.*

Erect Winter Fur Compared to Close Lying Summer Fur

When the hares are turning white a very noticeable feature is that the dark fur lies flatter than the white. In Fig. 32, Plate IV, a dark line shows along the fur over the spine. When the skin is spread out it appears as though a depression ran along the back. Fig. 33, Plate IV shows the reverse side of Fig. 32; the pigment in the skin coincides with the dark colored hair above. In Fig. 34, Plate IV, it can be seen that the dark fur lies closer to the skin than the white. As the erectness of the winter fur is coupled with the whitening process it seemed probable that some change in the skin was the cause of the alteration. A comparison was made between the growing hair roots and those which had ceased growing. As the living roots are sharply bent just above the bulb and the dead roots are perfectly straight, it was thought that this might have something to do with the erection of the hairs. It was found that the bend in the growing root is due to back pressure caused by the hair tip pushing against obstacles as it forces its way through the skin. In proof of this it will be noted that the bend is not always present and is variable in extent. Also, acute and irregular bends may be caused by drying and wetting the skin. It was assumed that the bend had nothing to do with the position of the hair above the skin, and also, as the root was below the skin, that it could not very well affect the hair outside. To determine how long the hairs grew under the skin before emerging, pieces of skin were examined under a low power microscope, and with a needle the hairs were bent at the point of emergence. The skin was then cleared and mounted and the length of hair shaft measured from the root to the bent portion. The average length of 30 hairs was 2.2 mm., the longest being 3 mm. and the shortest 1.3 mm. The new hairs grow parallel to the skin (see Figs. 5–11, Plate I). When the hair is white the hair roots have an entirely different shape; they have a brush-like termination and form a perfectly straight line with the hair. Instead of being anchored 2–3 mm. from the exit, the roots are then only 0.4 mm. from the surface of the skin (average of 20 roots), and nothing can be seen of the root sheath except bits of tissue sticking to the hair shaft just above the root, 0.2 mm. from the frayed end. These bits of tissue have the appearance of broken attachments and are to be seen on nearly all the roots. A probable explanation for the difference in distance from the root to the opening in the skin between the living and dead roots, is in the shrinkage of both the hair root and the skin itself. It is possible also that after the emergence of the new hair it may free itself from the skin by rising after desquamation of the epidermis, aided by the natural pull of the free end of the hair. And when the skin becomes thinner and tighter as it approaches the prime condition, the hair would become still more erect.

The marked differences between the living and dead roots at the time the skin becomes prime afford proof that the erectness of the winter fur is due to these changes.

Erectness of Summer Fur

It will be noted that in Table I three summer skins with erect hair are recorded. Though erectness has not been studied in summer hair as much

as in winter fur, it would seem likely that the cause is similar in both cases. It has been noted that the roots of summer hair are close to the surface, as they are in the winter skin. The flat summer fur shown in Fig. 32, Plate IV, is still growing. At an earlier stage of growth the hair would have been shorter still and closer to the skin.

Experiments on the Clipping and Dyeing of the Fur of Hares

The hair of four animals was clipped over one half of the body, including two feet and one ear. Before the results of the clipping are discussed it should be stated that cutting half the fur off an animal makes it uncomfortable, and must cause a strain on the system. The results of the experiments nevertheless show that both hair and pigment will regenerate, unless the clipping is done at a time when the hair roots have ceased to function. This happened in all cases with the ears and feet and no regrowth of fur occurred except on the soles of the feet. On the legs the growth of new fur was not as complete as it was on the flanks, so it is probable that depigmentation of the skin and hair in those regions was beginning.

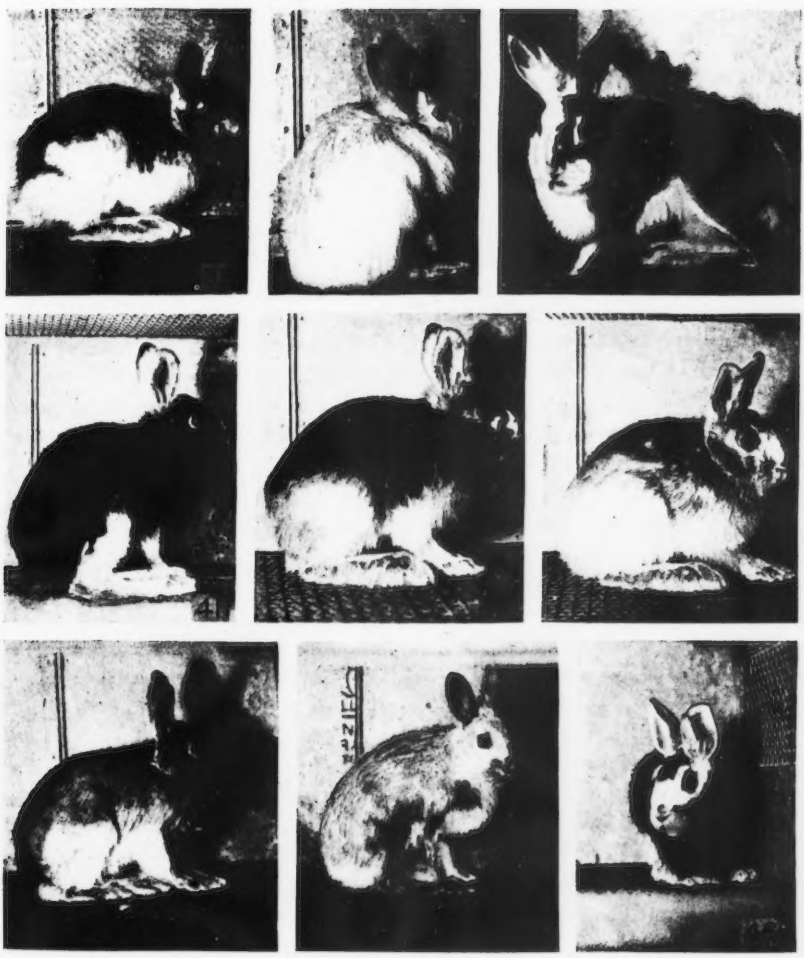
In three of the animals, Nos. 27, 29 and 30, a regrowth of fur from the existing roots took place. This fur was pigmented at first, and later it turned white, attaining about the same length as the fur on the unclipped side. Positive proof of this was obtained, as the ends of the hairs in Nos. 27 and 30 showed 100% cut ends. The final stage of growth was composed of a coat which was blue-black at the base, succeeded by fulvous, brown and white. The bands of color were not as uniform as on the unclipped side (Plate II, Fig. 18). Hare No. 29 grew a new coat which was blue at the base and had a buff colored layer above. The animal was killed at this stage (Plate V, Fig. 44). Above the buff were numbers of white guard hairs with cut ends. But both guard hairs and pile were present in smaller numbers than would be necessary to make the full white coat, the explanation being that the skin of the hare was beginning to whiten and the hair roots to die, especially the larger ones. A fourth hare (No. 34) was not clipped until the fur had completely whitened. Some of the blue underfur became rubbed off after clipping and the skin became bare in places. No regrowth of fur took place, except in three small spots, during 51 days, after which the animal was killed.

The clipping experiments have furnished proof that blanching of the outer parts of the hair occurs in the existing hairs, seeing that they can be identified by their cut extremities. The depigmentation of the fur is due to a destructive change.

Clipping Experiments

Experiment 1. Hare No. 27, captured at Cartier, Ontario, on May 12. On September 6 showed a definite whitening on the feet and legs.

Day 1: On September 16 the hare was white along the flank and part way up the hips and shoulders. Feet and ears were white. Skin not very dark but blackish over hips and shoulders. Was clipped on this date.



FIGS. 38, 39, 40. *Hare 34. This hare clipped after turning white. Note undercoat of blue-black fur. There was no growth of fur on the clipped side for a period of 51 days, proving that once the hair roots are frayed at the ends they cannot grow again.* FIGS. 41, 42, 43. *Dyed strip on shoulder. This strip disappeared, as shown in Fig. 43.* FIG. 44. *Hare No. 29. Buff colored coat.* FIG. 45. *Hare No. 35. Note bare ear and feet; no growth of fur occurred though the rest of the body became refurred, and later turned white.* FIG. 46. *This shows the sharp line between the brown fur and the white, as the change progresses.*

Day 10: The hair over clipped area, which grew after it had been cut, appeared to be pure white, but on closer examination in a better light it was found to be decidedly brown and a line along the back was quite dark.

Day 17: The forehead was dark brown, and back dark in color.

Day 19: The right ear which had been clipped was still brown and the hair short. The clipped feet and legs were blue and the hair was short. The hair on the clipped flanks was long and brownish.

Day 29: Legs blue up to stifle, shoulder and neck on clipped side. The brown line on the back which was noticed on October 14 had disappeared. The hair now appeared white.

Result. Day 30: Hare killed on October 18. The hairs on clipped side showed 100% cut ends. The coat was about 1 cm. shorter on clipped side.

Experiment 2. Hare No. 35, captured at Cartier, Ontario, on September 6. *Day 1:* Clipped September 26 on one side, including two feet and ear. Hair brown except a little white on ears and feet. White hair on forearm and tibia. After clipping, feet blue in color. Next to back, hair blue-black, skin pink. Blue-black color round eye, except for brown ring.

Day 21: Slight growth on clipped side of brownish hair. Unclipped side changing to white.

Day 27: Blue color round eye on clipped side turning brownish.

Day 36: Turning white round eye on clipped side. On unclipped side white, extending up hip and shoulder.

Day 46: Clipped side turning white, still brownish near backbone.

Day 53: Animal whiter.

Day 70: Animal white except clipped feet and ear, which had not changed color, and there was no growth of hair.

Day 86: No change.

Result. Day 112: Animal killed on January 15. On the clipped side the hair had grown as long as on the unclipped. The feet and ear were still bare and there was no regrowth of hair. The colored bands on the clipped side were not quite regular; the brown band below the white was missing, so that the coat was three-banded—white, fulvous and blue. All white hairs had pointed ends: they were new hairs. The skin was evidently prime when the clipping was done, and a new growth began 21 days later (Fig. 45, Plate V).

Experiment 3. Hare No. 29, captured at Cartier, Ontario, on May 12. *Day 1:* Was clipped September 26 on one side, including two feet and ear. Hare brown, feet and ears white.

Day 11: Slight growth on clipped side, of brownish color.

Day 21: Clipped side buff colored, hair ½ in. long. White guard hairs showing above buff coat had cut ends.

Day 23: Hare killed. Skin blackish, with yellow line over backbone. Under the microscope it was observed that the hair roots were beginning to die, especially the larger ones (Fig. 44, Plate V).

Result. A buff colored coat grew on clipped side.

Experiment 4. This experiment was made to ascertain whether any growth of hair would occur after the skin had become prime. Hare No. 34, captured at Cartier, Ontario, on May 12; began to whiten September 6; nearly white on October 23; pure white November 1.

Day 1: November 20, one side animal clipped, including two feet and one ear.

Day 21: Blue-black fur next skin had been rubbed off in places.

Day 31: Three small spots of hair grew on leg and nose. The largest spot about 1 cm. had a growth of white hairs tipped with black.

Day 51: Animal killed. No growth of hair except small spots mentioned above. Skin prime with few small black spots where hair had grown.

Result. It is quite clear that once the skin becomes prime in the autumn a regrowth of fur will not occur after clipping (Figs. 38, 39 and 40, Plate V).

Dyeing Experiments

Experiment 5. (Aniline blue.) Hare No. 30, captured at Cartier, Ontario, on May 12.

Day 1: September 26, a portion of the flank clipped. Aniline blue was rubbed onto the hair stubs and the skin. On this date, extremities white, nose white; white extending up legs.

Day 21: Animal nearly white.

Result. Day 23: Animal killed. Skin nearly prime; hair nearly white; on clipped patch hair not quite as long as on unclipped side.

Microscopic Examination of the Hair

The color bands were rather irregular (see Fig. 18, Plate II) but a regrowth occurred, a little shorter than that on the unclipped side. The hair was largely of kempy nature. All the fibres had cut ends tipped with blue (see Fig. 36, Plate IV), the remainder being white. It was evident that the dye which had colored the shaft of the hair stumps had disappeared. In a few hairs which had not whitened, and consequently had not lost their natural pigment, the dye adhered to the cuticle like a coat of paint, but the coloring was not as brilliant as at the tip.

Result. This experiment shows that there was a regrowth of hair from the original roots; that the hair became banded as before. It then whitened like the rest of the animal's coat. The clipping and application of dye identified the guard hairs and pile, and, as 100% were thus marked, the evidence is conclusive that the hairs whitened after they had finished their growth.

Experiments in which the Brown Hair was Marked with a Dye Before the Autumn Change to White

It was expected that the dyed hairs would remain colored after the surrounding fur had turned white. Dr. R. O. Hall of the Ontario Research Foundation kindly supplied the dye used in the experiments, namely, Clothfast Red GR. The dye was applied cold. The hair was combed over a card

and the dye applied; the hair was sponged with water afterwards to prevent the skin being burned. The dye colored the outer guard hairs and pile, the two brown layers and a little of the blue zone.

Experiment 1. Hare No. 28, received from Cartier, Ontario, on May 12.
Day 1: On September 16 two strips on hip and shoulder were dyed red. On this date the feet and ears were whitish; the rest of the body was brown.

Day 12: White extending on legs.

Day 26: White extending into dyed area. The hairs had the appearance of whitening under the dye.

Day 33: Dye almost gone. Animal whitening fast except for brown areas on backbone and head.

Day 34: Hare killed on October 18.

Result. As the dye had apparently disappeared, it was surprising to find that it was still present in its original coloring below the outer fur. The outer hairs, both pile and guard hairs, were white except for occasional hairs which had not yet lost their own natural pigment, and on such hairs the dye still adhered externally. The under fur, which normally retains its pigment when the outer coat whitens, was colored a vivid red. This would indicate that a hair which contains its pigment may be dyed, but that as soon as the hair whitens it will lose its own pigment and the dye as well. This implies that the dye had an external effect only, and had not penetrated into the hair. In the normal whitening of hair, it has been shown that a shiny cortical strip on the outside of a hair will produce a white coloration, if there is no colored material below it. In addition to this the whitened hairs showed evidence of degeneration as described in the section on winter coloration.

Experiment 2. Hare No. 34, received from Cartier, Ontario, on September 26.
Day 1: Strip dyed October 5 on shoulder and one hind foot. Hare had white ears and feet, otherwise brown in color.

Day 26: Nose turning white; depigmentation extending up legs.

Day 44: The dyed area had whitened for about ½ in.

Day 55: The white area had extended, surrounding the dyed strip.

Day 61: The dye had practically disappeared.

Day 71: As the dark strip along the back had not turned white, the ends of the outer hairs were clipped off and dye applied to a strip about 2½ in. wide. Dye was also applied to a patch of newly whitened hair on the flank. The hind foot which was dyed on Day 1 remained pink in color all through the experiment.

Day 92: Hare killed.

Result. The dyed patch on the shoulder had disappeared externally, as in Experiment 1 (see Figs. 41–43, Plate V). The underfur was still well colored with the dye. The patch of white hair which was dyed on Day 77 remained colored, as also did the foot which was dyed on Day 1. The clipped fur along

the back had whitened and at the clipped ends the dye had penetrated a little, so that each hair had a red tip (Fig. 37, Plate IV). The results confirm the previous results of clipping the hair before it turned white.

Discussion

As mentioned previously, the principal point which the writer desired to confirm was, as indicated in his previous paper (10), that the blanching of the fur in wild hares is due to a degeneration and partial depigmentation, and not to a replacement by pure white hair. The experiments show that the whitened fur still contains pigment at the tip and at the base, consequently it could not have grown in as completely white hair. The last of the fur to whiten is that on the back, where it appears isolated from the rest of the coat, and there is a delicate gradation from brown to white, with no appreciable shedding. The lengths of the brown and the whitened hairs are equal (see Fig. 17, Plate II). The results of the experimental clipping of the animals also furnish proof that the regrowth of hair whitened like the rest of the coat and could be identified by the cut ends. The results of the dyeing experiments furnish the same proof, the ends of the whitened hairs being marked by dyed tips.

The clipped hairs also showed color bands below the white tips, proving that pigment was being produced during their growth. The underfur stays pigmented throughout the winter in Ontario hares, so that the color bands remain. The only noticeable effect on the underfur caused by the whitening of guard and pile hairs is that they lighten the color of the bands a little. The white appearance of the guard hairs is deceptive because the parts of these hairs which are in the under coat appear whiter against the dark fur than they really are. These guard hairs contain large melanin granules, and therefore are not pure white. The pile hairs in the underfur are not visible because of their thinness.

Unexpected confirmation that the bleaching of the outer fur is due to an alteration in the nature of the hairs was obtained by dyeing them before they whitened. The dye disappeared as the hairs changed color, proving that there was a definite alteration in the cortical part of the hair. The underfur, which retains its natural shape and pigment, held the dye.

There is a close connection between the depigmentation of the hair roots and the bleaching of the hair above, and as soon as the roots have lost their pigment they cease to grow. It should be added that the white hairs are plainly dead and degenerating also; if they were of new growth, as some writers think, it would be expected that they should resemble new, well-shaped white hairs of the albino type. The writer believes, however, that a pigmented animal, such as the snowshoe hare, could not grow pure white hair except in regions such as the linea alba, or following some form of injury. Since the writer has found a "prime" condition of the hair roots in summer, similar to that occurring in winter skins, it naturally brings up the question why the hair whitens at one season and not at another. This cannot be

answered until more is known about the process underlying the change. But it can be pointed out that the bleaching occurs only in two kinds of hairs, the guards and the pile. The underfur and the tips of the ear retain their pigment, though both lose the pigment in their roots. Finally, it should be mentioned that the fur attached to the prime summer skins, such as were collected during the past season, must be shed before the autumn change to white. In all the skins examined during the change, the hair roots were in process of depigmentation, and this fact confirms what has been already stated, that the hair on these animals was of recent growth, because it is certain that once the coat has attained its full development the hair roots die and must be replaced by a new growth.

Since 1929 very few comments on the writer's work appeared, until 1932 when several articles were written by Grange (6, 7), Boyd (2–5) and Gunn (8, 9). Gunn was in general accord with the writer's ideas on the whitening of the autumn fur. Grange differed from the main conclusions. Grange's two papers deal with the color phases in hares and also with protective coloration. He adheres to the idea that new growth of variegated, white tipped hairs replaces the summer coat. He says, "It is not a question of a black pelage, for example, being replaced by a white one but rather involves the replacement of one variegated pelage by another variegated pelage." If Grange's explanation is correct, that a new growth of white tipped hairs takes place in the autumn after the moult, it implies that the new hairs start growing as white hairs, and if so, we should see pure white underfur prior to the outward whitening of the animals. Grange's explanation of the change to white is unsupported either by figures of the hairs, or by mention of the hair roots or the skin in which such changes come.

Boyd (5) makes the following statement: "The seasonal whitening which takes place in such animals as *Lepus americanus* has been ascribed to an acute and complete bleaching of the pigment granules themselves (Hadwen, 10) and not to the shedding of the coat as a whole. Atmospheric oxygen is powerless to produce such an exaggerated change, and since there is no known connection between the living body-cells and the wholly dead keratinized cells of the fibres, it is difficult to reconcile these facts with the theory. It is more probable that the whitening is due to the gradual replacement of the old coloured coat by a new white one without mass shedding of the coloured coat as a whole." The writer wishes to correct the opening sentence in which he is misquoted, as he did not state that an acute and complete blanching of the pigment granules took place, but that the whitened hairs still contained pigment in certain areas and that they were not of new growth. Another conclusion of Boyd's which may be attributed to the writer is that atmospheric oxygen produces this exaggerated change. It is well, therefore, to state that there was no suggestion of this sort in the writer's paper (10). As to the replacement of the colored coat by new white hair, Boyd proposes this solution of the problem without giving any experimental support of the idea.

Acknowledgments

The author wishes to acknowledge his indebtedness to Dr. H. B. Speakman, Director of the Foundation, for advice and helpful criticism; to his colleague Mr. A. M. Fallis for the drawings in this article, and for willing and valued help in the experiments; to Mr. Elmer Craine, Messrs. J. Larkin and J. Bailey for their many courtesies and help in securing live hares which made the investigation possible; to Dr. R. Law and Mr. D. A. MacLulich for fetuses and hare skins; to colleagues in the Foundation for many helpful suggestions; and to Mr. J. E. Pritchard, animal keeper, who has been successful in keeping the hares healthy in captivity; and to Mr. R. A. Stockhill for the photos in Plate II.

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ADDITIONAL OBSERVATIONS ON SOME UTRICULARIACEAE[1]

By Francis E. Lloyd[2]

Abstract

In previous papers by the author several types of traps of *Utricularia* have been described; in the present the trap of *Biovularia* (very closely akin to *Utricularia*) is described and found to be a distinct type, combining in itself characters of the two previously known, described traps of the types *vulgaris* and *purpurea*. In the species *U. tubulata* v. Muel., which is a freely floating form not suspected previously of having a trap of structure other than that of *U. vulgaris*, it is shown that it conforms with that of the Australasian "land" species *U. manziesii, dichotoma*, etc. *U. tubulata* is an inhabitant of N. Queensland also.

In place of the rather easily accepted idea, expressed even by Goebel (1) that the floating forms are all alike, we now know of three distinct types, represented by the species, as types of their groups, *U. vulgaris, U. purpurea* and *U. tubulata*.

Since the publication of my recent paper, being the Presidential address (7) before the Section of Botany, British Association for the Advancement of Science, Leicester meeting, 1933, opportunity better than that previously available has been afforded for the study of material of the genus *Biovularia* and of a species of *Utricularia* collected by W. E. Armit in the mountain swamps about Rockingham Bay, Queensland, and described by F. v. Mueller as *U. tubulata* (9). True, this material was in the collections of the British Museum at South Kensington, and herbarium specimens are at best not very serviceable for such purpose as the present; nevertheless I have been able to make out quite clearly certain critical points of structure which justify the following notes, awaiting, with the favor of fortune, adequately preserved specimens of these interesting plants. I am indebted to the Authority of the Science Museum Herbarium for permission to take minute but, as the event proved, sufficient material for my present purpose.

Dried specimens of the traps of these plants do not recover their original form, so far as my own methods of treatment go; but traps which have by chance been pressed laterally and symmetrically are often sufficient to enable one to identify them as belonging to one or other of the types already described by me (2, 3, 7), or to permit the recognition of an additional type, as in the case of *Biovularia*. It cannot be claimed that the descriptions below can be pushed too far in the matter of detail, only that they are substantially correct.

What has been said in previous publications (2, 3, 7) will enable the interested reader to follow these notes without a lengthy recapitulation of the general characters of the *Utricularia* trap*. Those with which we are here concerned are the form and anatomy of the door or valve and of the threshold. If these can with certainty be characterized, even though not exhaustively described, it is sufficient. It is, of course, important to observe the velum,

[1] *Manuscript received March 16, 1934.*
Contribution from the Department of Botany, McGill University, Montreal, Canada.
[2] *Macdonald Professor of Botany, McGill University.*
**See particularly References 2 and 3.*

but this is rather too much to expect unless properly preserved material is at hand. That the velum is present, however, may be inferred from the histology of the pavement epithelium of the threshold.

Utricularia tubulata

This is a submersed floating plant of the general appearance of *U. vulgaris*, judging from the herbarium specimens as they lie before the eye, but from the description of F. v. Mueller (9), "The leaves capillary-linear, segments of the leaves verticillate and with many ascidia", it may be inferred that the plant more resembles *U. purpurea*. So far as I can make it out, however, the traps are supported on lateral stalks and this does not accord with the latter. Since it is a floating form, I had earlier rather supposed it to resemble, in the form of its trap, *U. vulgaris*, judging from a fragment of material kindly sent to me by Dr. A. B. Rendle. Additional material (three traps only) showed that this supposition was wrong; nor does the trap resemble that of *U. purpurea*, but most interestingly the form aligns itself with that of the traps of certain other Australasian species, all, however, so far as we know, of the so-called terrestrial habit. From the point of view of the questions of the origin and geographical distribution of the Utricularia, this fact is of paramount importance.

The alliance of *U. tubulata* with the type of *U. hookeri* (3) or of *U. monanthos* (7), etc. is first of all indicated by the form of the trap and its appendages (Figs. 1, 2; Plate I—1–4). In lateral view it is oblique and semicircular with a longish stalk at one end. At the other end arise three long unbranched appendages, one and one-half times as long as the trap. One of these is central, arising from the middle point of the overhang of the entrance, and corresponds to the rostrum found in *U. monanthos*, *U. menziesii*, *U. dichotoma*, etc., but is enormously elongated. On each side, above the entrance, is another quite similar appendage, so that the trap has two long "antennae" and a rostrum, making three processes extending forward for the distance indicated (Plate I–1). There are no other appendages, in this departing from the type *U. monanthos*.

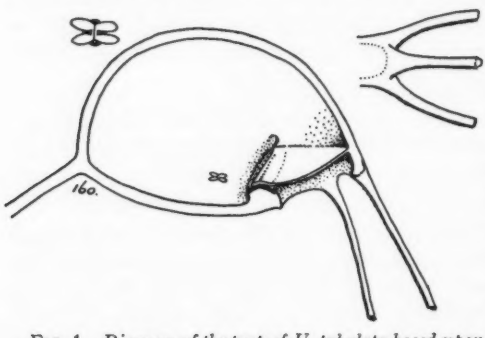
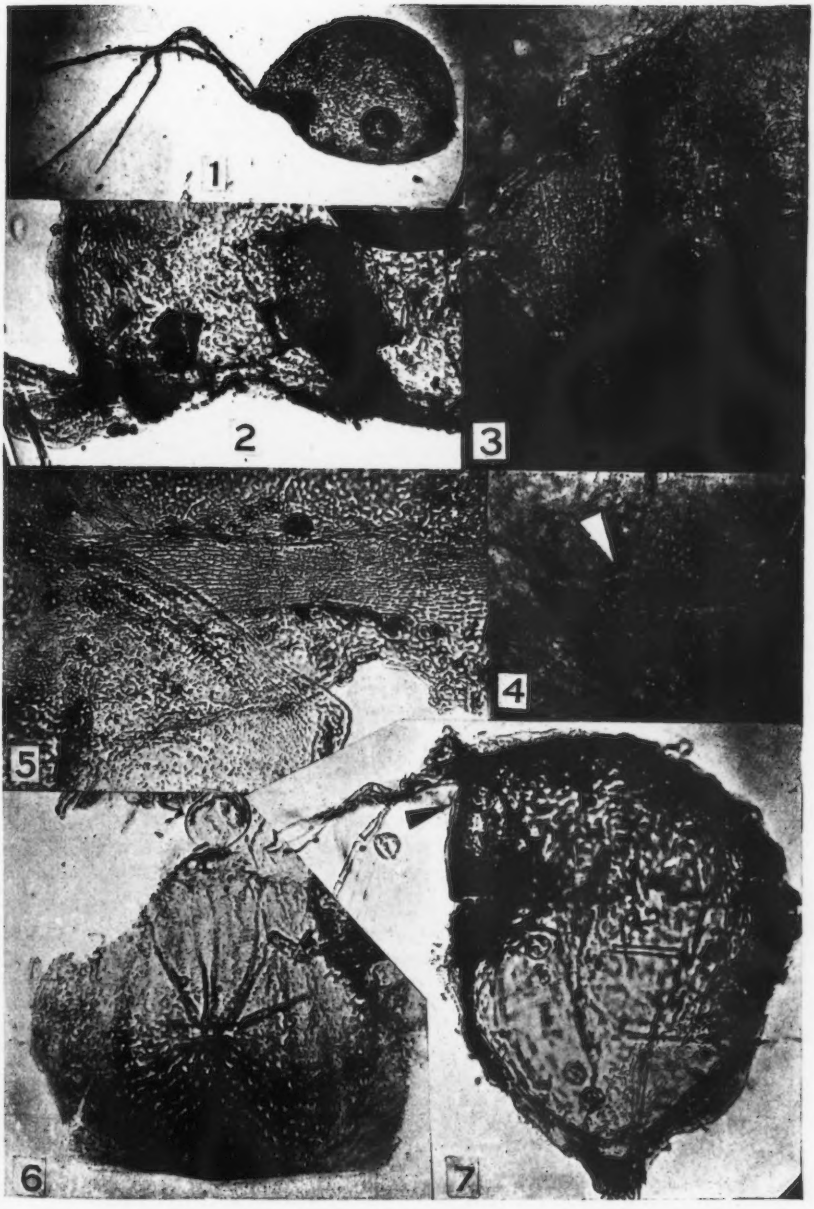


FIG. 1. *Diagram of the trap of U. tubulata based upon an interpretation of Figs. 1–4 in Plate I. Upper left, a quadrifid trichome; right, the front of the trap from above.*

The profile of the door and threshold are revealing. This can be seen in a symmetrically compressed trap after clearing (Plate I–2; Fig. 1). The door makes a long arch, curving downward and backward in a manner quite as I have represented for *U. dichotoma*, etc. It can be seen (in sagittal optical



FIGS. 1–4, *Utricularia tubulata;* FIGS. 5–7, *Biovularia.*

FIG. 1. *Lateral view of the trap, with long rostrum and two antennae.* FIG. 2. *Entrance of the trap, showing the silhouette of the door (indicated by three pointers) and the threshold on the right.* FIG. 3. *One-half of the threshold, the forward zone of which is overlain by the edge of the door, seen as a veil, the edge running up to the inner angle of the threshold. The right and left orientation of this picture is the opposite of that of Figs. 2 and 4. From an infra-red negative.* FIG. 4. *Detail of Fig. 2 showing something of the structure of the threshold (optical section) and the edge of the door (indicated by the pointer) out of position through shrinkage. Infra-red negative.*

FIG. 5. *Half of the threshold and of the door-edge of Biovularia.* FIG. 6. *The door from in front.* FIG. 7. *The entire trap, lateral view. The tripping bristles lie against the upper half of the door and are indicated by the pointer.*

section) to be of uniform thickness, true of no other type of trap, and to meet the threshold at a very narrow angle (7). The latter is evidently ridged (Plate I—3–4), and it can be inferred that the lower free margin of the door (Plate I–4) overlies the elevated middle zone (ridge) of the threshold. This structure is, however, sadly contracted and distorted in the specimen, but its expectedly more firm and resistant marginal zone could be clearly seen in an infra-red negative (Plate I–4). Another trap afforded on dissection a fairly clear picture of the pavement epithelium for the extent of one-half the length of the threshold (Plate I–3). This most resembles that of *Polypompholyx* (Fig. 2) but that need give us no cause for pause, as this plant conforms with *U. menziesii* in the general character of the entrance mechanism —that is to say, the threshold is not the very wide affair (in the fore and aft

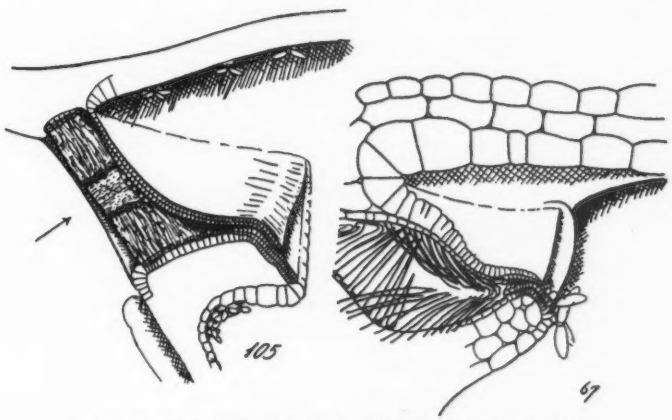


FIG. 2. *Left, U. hookeri; right, Polypompholyx multifida. For comparison with Fig. 1.*

sense) of *U. menziesii*, *U. monanthos*, etc. for the silhouette (Plate I–2) indicates a narrower platform in front of the zone of actual contact between the door and the threshold. It is from this platform that the velum springs. but, though I have not been able to see it, I have been able to get some indications of a velum *above* the entrance, again as in *U. menziesii*, etc. The velum would seem to be of the circular kind of this species and its allies (Fig. 2–105).

The evidence observable therefore supports the view that the trap of the floating species, *U. tubulata*, conforms to a strictly Australasian type to which belong also *U. menziesii*, *U. dichotoma*, *U. volubilis* and *Polypompholyx* (two species), so far as my observation goes. Among the total of the species of the floating submersed habit, therefore, we can recognize at this time three types, represented by *U. vulgaris* and its allies, the *U. purpurea* group, and *U. tubulata*, which may not be unique, however.

It may be noted here that the character chosen to support the specific name is the inflation of the flower-scape, which we may suppose makes it

act as a spar-buoy, helping to support the flowers above the water surface. One other species, *U. warmingii* of the New World, has this feature, as described by Merl (8).

The interior surface of the trap is armed with many quadrifid trichomes, the arms of which are short and thick and lie parallel instead of spreading (Fig. 1). I can find no bifid trichomes in the usual position, that is on the inner surface of the threshold, but this may be owing to failure of preservation.

Biovularia

This is a monotypic genus, diagnosed by Kamienski, inhabiting eastern tropical America. A submersed floating plant, it has the habit of *U. vulgaris* or *U. purpurea*, with a leaning toward the latter.

The trap stands upright on its stalk and shows but little, if any, obliquity. In lateral view, it is broadly pear-shaped, somewhat flattened on the side of the entrance (Fig. 3; Plate I–7). Each of the upper angles of the entrance bears an antenna which resembles that of *U. vulgaris* but extends forward with a downward curvature as in *U. gibba*.

The door, though conforming to a more fundamental type which would include that of *U. vulgaris*, differs so much from this as to set it apart as unique. Its tripping bristles are five or six in number (instead of normally four in *U. vulgaris*, etc.) and are inserted at, or just below, the middle point of the door as seen in sagittal section, in this resembling *U. purpurea* and not *U. vulgaris*. The lower half of the door in its middle reach is therefore the middle piece and it is uniformly thick and massive. The thickness is fairly uniform and it has curvatures which, if slight, are characteristic and can be better appreciated by a glance at Figs. 3 and 4–*B*. The upper half is the outer hinge, and is thinner with a slight S-shaped curvature, the concave element being the more pronounced. It almost duplicates the condition of *U. purpurea*. The tripping bristles are so inserted that their bases, in contact with each other, form a crowded transverse row. While the recognition of a central hinge is difficult if not impossible in dried material, even after treatment and clearing, the fact that in this kind of material the bristles are always laid up against the outer hinge (Plate I–7) indicates a ready movement in this direction, at least, in the living trap.

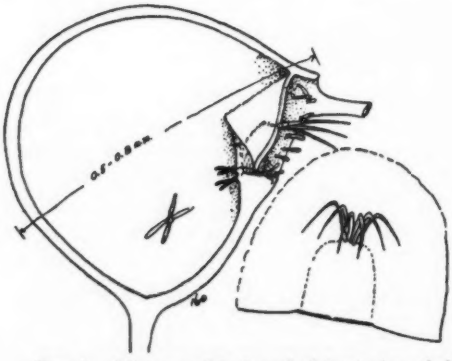


FIG. 3. *Diagram of trap and of front view of the door (right) of Biovularia violacea Kam. The middle piece of the door is below the tripping bristles and is indicated by a surrounding broken line.*

Their mode of insertion and form are quite as in *U. vulgaris* and there is no knob-like protuberance as in *U. purpurea.*

When the door is examined *en face* (Plate I–6), it is seen that its anatomy is practically identical with that of the door of *U. purpurea* (5) in regard to the proportions and directions of the component cells. As just mentioned, however, there is no knob, and the beading along the free edge of the door, seen in *U. purpurea,* is also absent. The middle piece is indeed somewhat

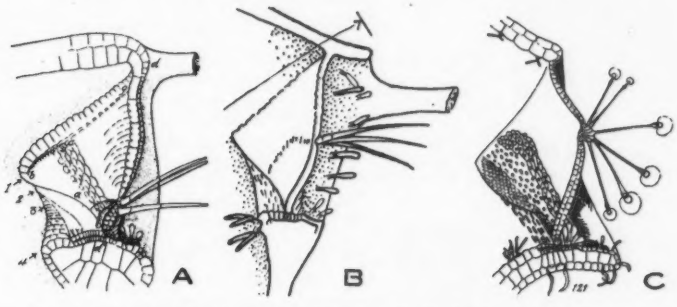


FIG. 4. *A, U. vulgaris; B, Biovularia; C, U. purpurea, for comparison. In A, in a strictly sagittal section, only two bristles would show.*

more massive, and is applied to the threshold in a wider angle than in that species, having therefore a more direct thrust against the pavement epithelium (7), so that the velum readily adjusts itself without any further assistance.

The threshold is of the type in *U. vulgaris* (4) in shape and in structure of the pavement epithelium (Plate I–5). A slight matter of difference is found in the fact that it lies somewhat as in *U. subulata* (Fig. 5) or in *U. resupinata* (2) and rather more forward than in that species, so that, as mentioned above, the thrust of the door is approximately normal to the plane of the pavement epithelium. The inner wall of the threshold bears a few bifid (?) trichomes, while the inner wall surfaces bear quadrifids with rather long spreading arms. The number of these hairs is small in contrast with the *vulgaris* or *purpurea* type.

It will be seen that the trap of *Biovularia* is a curious mosaic of structures apparently derived from *U. vulgaris* on the one hand and *U. purpurea* on the other (Fig. 4). While the former is cosmopolitan, it has closely related American species, and the latter is confined to the New World. If one dared to speculate beyond the evidence, one might make out a case for the origin of *Biovularia* as a hybrid. At all events, the facts as known are suggestive.

Briefly summarizing, it has been shown that the trap of *U. tubulata,* a submersed floating form, conforms to a type which is confined to Australasia,

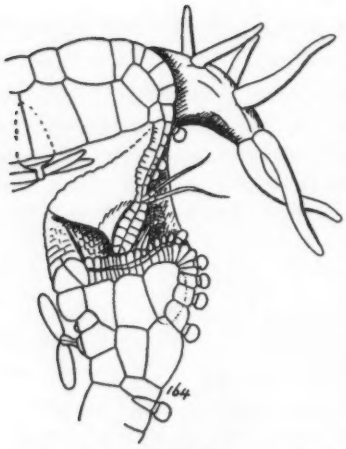


FIG. 5. *U. subulata. Diagrammatic representation of a sagittal section of the entrance. (Preserved material kindly supplied by Prof. J. C. Th. Uphof.)*

of which *U. monanthos*, *U. menziesii*, etc., have been taken as exemplars. The relation in phylogeny of these is analogous, one may argue, to that between the *U. vulgaris* type and certain terrestrial forms, such as *U. subulata* (Fig. 5); that is, there are corresponding terrestrial and submersed forms which can readily be conceived as having followed parallel courses of evolution.

Biovularia offers a trap with such structure that it stands alone as unique and therefore adds a type to the list already established in my previous publications and making a fourth member of the floating series above mentioned. It appears to be a mosaic of characters of two types, exemplified in the type of *U. vulgaris* on the one hand and of *U. purpurea* on the other.

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A BIOMETRIC STUDY OF THE CULMS OF CEREALS AND GRASSES[1]

By Henri Prat[2]

Abstract

Many attempts have been made to use absolute biometric values as accessory specific characters in cereals and grasses. The present note is an attempt to express by plain graphs not only the absolute average lengths but also the relations of length between the internodes of the culm.

In some cases, the graphic representation leads to a simple mathematical formula; in others this is not possible, but the shape of the graph gives interesting information on the role played by the young inflorescence during the growth of the culm. Sterile or, on the contrary, hypersexual culms have the history of their youth inscribed in their adult structure.

The observations in the present paper will be connected with a larger study of the conditions of growth and mode of differentiation of the plant tissues. Relations with the peculiar structure of the epidermis of the culm are discussed.

I. Increasing Size of the Internodes of a Cereal Straw (Biometric Gradation)

It is a conspicuous fact that the internodes of cereal straw increase regularly in size from the base to the top. This peculiarity seems to be an expression of the special polarity of the stem, caused by the presence of the ear at its apex; that is to say, a biometric form of the *gradation* (3, p. 199) noticeable also in morphological, anatomical and histological features (5, p. 165).

Let us consider, for example, a plant of Einkorn wheat (*Triticum monococcum*). The length of the internodes of the 10 straws forming the tuft are shown in Table I.

TABLE I

Lengths of internodes of the 10 straws forming a tuft of Einkorn wheat

Internode	Straw										Average lengths, cm.
	I	II	III	IV	V	VI	VII	VIII	IX	X	
	Length of internode, cm.										
7	436	472	190	357	193	294	313	162	340	359	311.6
6	209	221	132	177	124	171	177	99	203	210	172.3
5	95	90	56	82	60	95	91	73	88	100	83
4	25	25	38	40	24	60	56	65	50	64	44.7
3	10	12	15	9	4	38	31	23	16	25	18.3
2	5	—	5	5	—	14	6	5	5	10	5.5
1	—	—	—	—	—	8	2	1	—	4	1.5
Total length	780	820	436	670	405	680	676	428	702	772	636.9

[1] *Manuscript received March 13, 1934.*
Contribution from the Department of Biology, University of Montreal, Montreal, Canada.

[2] *Director of the Department of Biology, University of Montreal.*

For purposes of comparison the top internodes of all the stems are given the number 7, this being the number of elongated internodes on each of the principal culms. The second internode from the top is number 6, and so on. On this basis the sizes of the successive internodes are plotted on Fig. 1 and the lines join the points representing the internodes of each culm. While there are irregularities, notably in the cases of minor culms III, V and VIII, the broken lines follow a concave and upward path. The curve *M* representing the average size of the internodes is more regular than the curves for individual stems since the small differences due to the conditions of growth peculiar to each stem are levelled out.

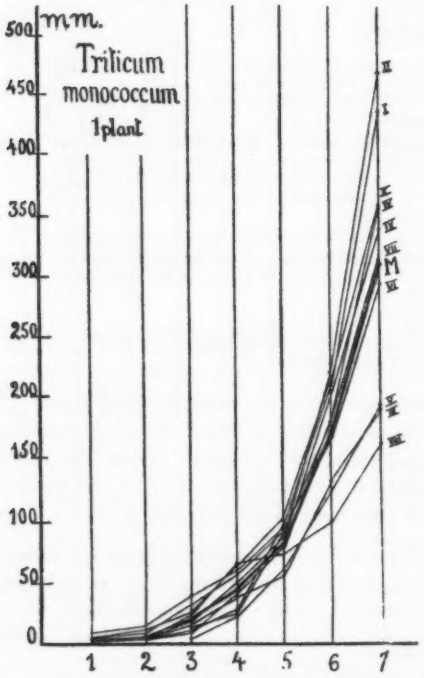

FIG. 1. *Relation between the lengths of internodes of a plant of Einkorn wheat (10 straws) and their numerical rank, plotted according to the ordinary system of co-ordinates. The heavy line M represents the average values.*

Many attempts have been made to express by a simple formula the phenomenon of the increasing size of the internodes. Novacki* states that "the length of each internode is the arithmetic mean of the lengths of the internodes immediately above and below it". Lloyd (2, p. 3) says "the terminal internode in wheat is 50 per cent of the whole straw in length and over twice that of the subterminal internode". But those expressions have only the value of a practical rule, which does not always coincide with reality, and cannot lead to an interpretation of growth.

An attempt has been made here to develop a more significant expression of the biometric gradation of internodes and this has, in some cases, been successful.

II. Mathematical Expression of the Biometric Gradation in Some Straws

In Fig. 2 a logarithmic scale has been used, the ordinates representing length of internode. The curve in Fig. 2 *A* is based on the same data as curve *M*, Fig. 1, and represents the averages for the 10 culms listed in Table I. Fig. 2 *B* is based on 20 culms from two plants of the same strain of *Triticum*

*See References (4, p. 63) and (1, p. 67).

monococcum. The obvious tendency of the points to fall on a straight line, most marked in Fig. 2 *B*, indicates that chance is not an important factor.

The equation expressing this relation is:

$$\log Y = K \log n + \log A \quad (1)$$

where Y is the length of an internode; n, its numerical order; K, the slope of the straight line; and A, a constant. Therefore:

$$Y = A\, n^K, \quad (2)$$

which is an expression of the length of the internode as a function of its numerical rank.

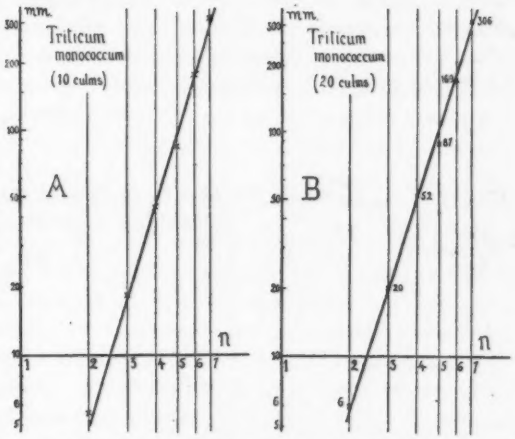

FIG. 2. *Relation between the lengths of internodes and their numerical rank, plotted on a logarithmic scale. A. Average lengths of the internodes of the 10 straws considered in Fig. 1. B. Average lengths of 20 culms of two plants.*

To obtain the value of K, we can substitute the lengths of two internodes, for example, 2 and 7, in the formula:

$$K = \frac{\log Y_7 - \log Y_2}{\log 7 - \log 2},$$

from which we obtain (from data in Fig. 2 *B*)

$$K = \frac{\log 306 - \log 6}{\log 3.5} = \frac{2.48572 - 0.77815}{0.54407} = 3.135.$$

The exponent K gives the slope of the curve, that is to say, the *rate* of increase in size from one internode to the next. We can take it as an expression of the average *biometric gradient* of the culms.

A is then obtained from Equation (1).

$$\log A = \log 306 - 3.135 \log 7.$$

The length of a given internode, Y_3, may be calculated as follows:

$$\begin{aligned} \log Y_3 &= 3.135 \log 3 + \log 306 - 3.135 \log 7 \\ &= 3.135 (\log 3 - \log 7) + \log 306 \\ &= \log 306 - 3.135 \times 0.3680 \\ &= 2.48572 - 1.15368 = 1.33204, \end{aligned}$$

from which, $Y_3 = 21.8$. Actually $Y_3 = 20$. Similarly

Y_4, calculated, $= 52.95$. Actually, $Y_4 = 52$.
Y_5, calculated, $= 106$. Actually, $Y_5 = 87$.
Y_6, calculated, $= 188.8$. Actually, $Y_6 = 169$.

The graphs obtained for isolated straws are far less regular than those obtained with mean values for a large number of straws. The individual fluctuations of the internodes may reach 50% of the average value and sometimes a given internode may even be smaller than the internode immediately

below it. Therefore the formula $Y=An^K$ gives in individual cases only a rough approximation. However, the comparison of many straws belonging to the same plant may give rise to interesting information, and the most valuable element of the formula is perhaps the expression of the gradient K.

It will be observed that the principal stem has the greatest slope and highest exponent K; then come the secondary stems; then the tertiary stems with the lowest value of K, as far as it is possible to consider a direction for the line joining the irregular points obtained with the small straws.

III. Comparison of Some Cereals and Grasses in Regard to the Biometric Gradation

A. *Cereals*

The mathematical relation shown above does not apply to every case. However, the writer has found it to be an approximate expression of the biometry of straws in many cereals. For example, in specimens of Spelt (*Triticum spelta* L.), very regular in shape, as many as six points were obtained in a straight line (Fig. 3 *A*), a fact which excludes, as in the case of *T. monococcum*, the hypothesis of the effects of chance.

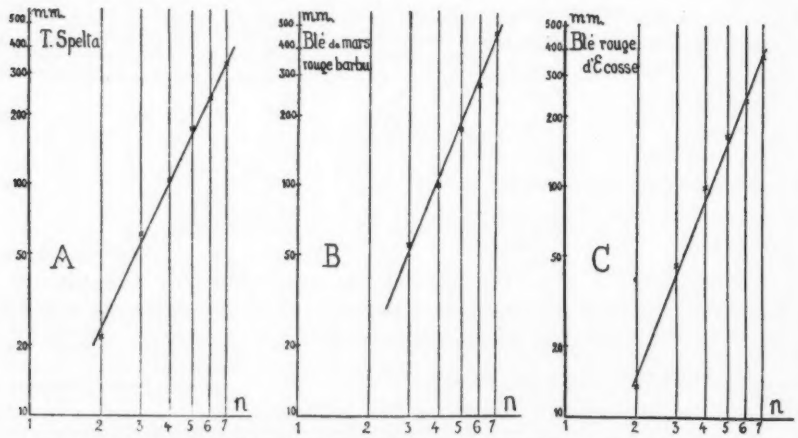

FIG. 3. *Logarithmic relation between the lengths of internodes (average values) and their numerical rank. A. Triticum spelta—11 culms. B. Blé de Mars rouge barbu (T. vulgare ferrugineum)—12 culms. C. Blé rouge d'Ecosse.*

With some wheats of the group *T. vulgare*, for example, on "Blé de mars rouge barbu"; (*T. vulgare ferrugineum* Korn.), Fig. 3 *B*, and on "Blé rouge d'Ecosse" (*T. vulgare milturum* Perc.), Fig. 3 *C*, the law can be verified in a satisfactory way. In general, the five upper internodes are elongated and can be used for the establishment of linear graphs. But in other varieties or species the conditions are entirely different. Consider, for example, the graphs for a sample of Miracle wheat (*T. turgidum mirabile* Korn.), Fig. 4 *A*. In this case the internodes 2, 3, 4, 5 and 6 give points regularly enough disposed on a straight line. But the last internode (No. 7) is placed distinctly

above the line traced by the inferior internodes. It seems that, in this case, a hypertrophic and abnormal elongation had affected this upper internode during its growth. We can attribute this fact to a sort of "hypersexuality" of the plant. A similar peculiarity was found with wheats of the group "Amidonnier" (Fig. 4 *B*), (*T. amyleum* Ser, *dicoccum* Schübl), and it seems rather frequent in the species *turgidum* and its varieties. Analogous facts appear in the study of annual wild grasses.

It is clear that, even when it is impossible to recognize a regular mathematical rule, a logarithmic graph can give interesting information on the species examined. Thus, when the plant is grown under sufficiently normal conditions, and when the average is based on a number of straws sufficiently large to eliminate individual fluctuations, the *shape* of the graph can express characteristic features of the plant. The shape of the curve would be more useful than the absolute measurements which are often used as systematic characters (3, 4); since absolute sizes are more directly affected by external conditions, whereas the shape of the graph expresses, to a great degree, the reciprocal internal influence (interactions) of portions of the same stem during growth.

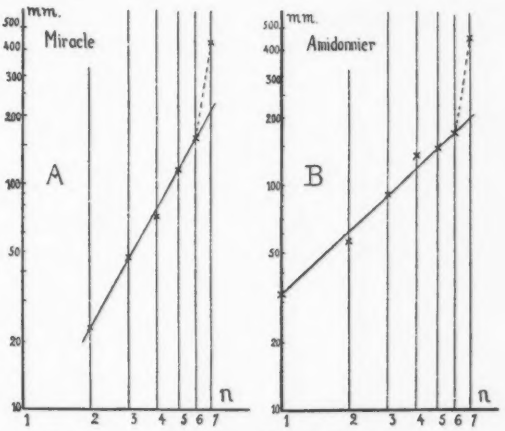

FIG. 4. *Logarithmic graph—A. Miracle wheat. B. Amidonnier.*

Other cereals than wheat, *e.g.*, barley (*Hordeum*) show biometric characters with the same types of gradation as the wheats mentioned.

B. *Wild Grasses*

Wild species of grasses show characters similar to those of the cultivated cereals.

In the logarithmic graph for a straw of *Poa nemoralis* (Fig. 5), the seven upper internodes give points in a straight line, a good verification of the formula. The aerial and reproductive parts of its stem are thus built according to the same general rule as a cereal straw. But it is worthy of notice that, in the perennial species, the basal part, which is characterized by the presence of lateral shoots and short internodes, shows no definite law of length. In this inferior vegetative portion, the elongation is governed only by the antagonism of growth between internodes and shoots, by the importance of rooting of the nodes, etc.

Regularity of shape allowing the detection of a mathematical law is subject to the condition of *absolute freedom* of the axis; that is to say, the total absence

of shoots or roots which introduce a disturbance in the adduction of sap and cause the irregular growth of meristems.

Of course, in a cereal, the basal internodes, in the tillering part of the stem are also absolutely irregular and are therefore in the same class as the rhizomes of a perennial species.*

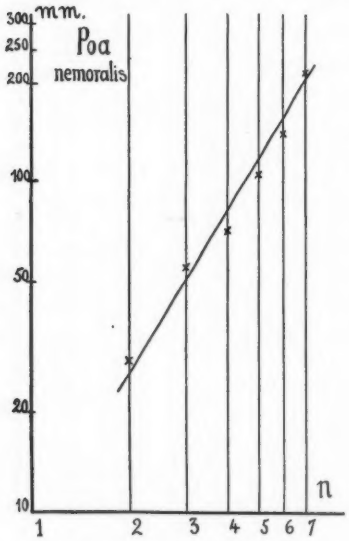

FIG. 5. *Logarithmic graph—Poa nemoralis.*

C. *Sterile and Perennial Stems*

A peculiarly interesting case is presented by the sterile shoots of some grasses. When a stem has no ear, or more generally no inflorescence, at the apex, the regularly increasing size of internodes described in preceding cases is not observed. For example, in the sterile shoots of *Holcus lanatus*, the internodes near the middle are of about equal length, and there is a progressive decrease in size towards the apex.

A most striking case is given by the stems of bamboos. These big perennial straws develop their entire growth in a single year, and their apex is, in general, entirely devoid of any trace of inflorescence. The flowers appear only on lateral branches, long after the perfect consolidation of the main stem. It should be noted, also, that all the internodes of a bamboo, above the short, rooting basal pieces, are of rather uniform size in the middle of the stem. Moreover, in the upper part, they show a regularly decreasing length towards the apex, exactly the reverse of what occurs in the fertile culms previously referred to.

This observation confirms our supposition that the biometric gradation of the culms is caused by the floral influence. And further confirmation is given by the fact that lateral flowering branches of the Bambusae show, frequently, internodes of increasing size, (*e.g.*, *Chusquea quila*, *Arundinaria hindsii*). Those fertile shoots are built on the same pattern as an entire straw of an annual grass.

The writer has indicated in another publication (5, p. 304) that the main stem and leaves of bamboo are deprived of any gradation in the structure of the epidermis. Histological and biometrical gradation, both being effects of the same cause, are thus in perfect correlation.

D. *Annual Grasses*

At the other extreme of biological conditions are the small short-lived annual grasses, such as *Mibora verna*. The logarithmic graph based on this

By basal node or internode is meant the inferior part of the plant which bears roots and is usually underground. Some of these may conform to the logarithmic relation shown by the upper ones but, as many irregularities occur, it is preferable to avoid a general statement for them.

plant (Fig. 6) is a very simple one, because only a few internodes are somewhat elongated during the few weeks of the vital cycle of the plant. The lengths of the internodes are: 88, 5.5, 1.5, 0.7, and 0.4 millimetres. The three points given by the upper internodes are not on a straight line and the broken line of the graph is strongly curved upwards. The last internode is relatively enormous compared with the others, and we have a case resembling to some extent that of "hypersexual" wheats, such as *T. mirabile* and *T. amyleum*, where the upper part of the straw becomes hypertrophic by sexual influence.

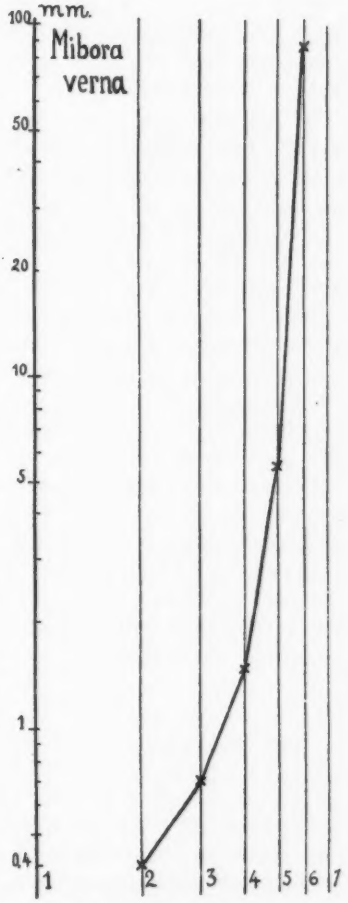

FIG. 6. *Logarithmic graph—Mibora verna.*

The influence of the maturing inflorescence is a dominant one. In *Mibora* also, and to an even higher degree, all the parts of the small and weak vegetative system are exhausted by the reproductive function, and life ends after a very short time.

The writer has pointed out elsewhere that, in *Mibora verna*, the histological differentiation of the epidermis is one of the lowest degree existing among grasses (5, p. 276). In this regard, too, *Mibora* is the opposite of the bamboo with its perennial, highly differentiated stems.*

The peculiarities of annual short-lived grasses may also be compared with differences noticed in cultures of the same cereal sown in the autumn and in the spring, *e.g.*, *Triticum monococcum*. The curves based on straws of the stock sown in the fall have slightly less slope than those based on straws of the spring stock; the exponent K of the formula is smaller.

The biometric gradation is therefore increased when the vital cycle is shortened.

Summary

1. The possibility of expressing the relations between the lengths of internodes of the culms of many species of grasses by a simple graphic representation in logarithmic co-ordinates has been demonstrated.

**The word "gradation" expresses a comparison between two parts of the same organ; the word "differentiation" expresses a property of a given area. Therefore histological gradation may, or may not, occur along a highly differentiated, or a slightly differentiated culm, if both are of uniform structure.*

2. In certain cases this graph takes a linear form which may be represented by the relation

$$Y = A_1 n^K,$$

giving an approximate expression of the length Y of the internodes as a function of their numerical rank, n; K being an expression of the *biometric gradient* of the culm.

This relation, only roughly approximate for isolated culms of those species, becomes more accurate with average lengths calculated on a great number of straws, particularly on principal culms, in genetically pure strains, and under regular conditions of growth.

3. In other species or varieties the preceding rule does not apply. However, the logarithmic graphs afford valuable information, for the shape is often characteristic. For example, in some cases the upper internode is hypertrophied and its apical point is placed high above the line obtained with the points representing the basal internodes. This condition is shown in particular by some wheats with strong sexuality: *T. mirabile*, *T. amyleum*. Further experiments will be made to find in what measure this abnormality is an hereditary and constant character, and in what measure it can be changed by conditions of growth and environment.

4. Small short-lived annual grasses, such as *Mibora verna*, also show an hypertrophy of the upper internode. In general, the biometric gradation is increased when the vital cycle is shortened.

5. When a culm is deprived of inflorescence at the apex, as in the bamboos, it does not show the regularly increasing size of internodes (biometric gradation) characteristic of fertile culms. This peculiarity may parallel the absence of anatomical and histological gradation in those stems.

Conclusions

Culms of grasses are very suitable material for the study of the influence exercised by sexual organs on the growth of an articulated stem.

The whole history of this influence is inscribed in the structure of the adult straw and the writer intends to show subsequently the relation existing between these observations and the dynamics of growth.

Gradation means the presence of an inflorescence at the apex of the growing stem; regularity means freedom of growth of the axis. Thus, biometric gradation is only a form of the general polarity which appears in many anatomical, histological, and physiological features of the culms of grasses.

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A PHOTOELECTRIC CELL METHOD OF MEASURING THE VELOCITY OF PROJECTILES[1]

By D. C. Rose[2]

Abstract

The velocities of rifle bullets have been measured by causing the bullet to interrupt successively beams of light shining on photoelectric cells. The resulting current pulse in the photoelectric cells, after being amplified, actuates a recording device. Two methods of taking the records were used. In the first the amplified current from the photoelectric cells is recorded by an oscillograph consisting of an Einthoven galvanometer and a rotating drum camera. In the second method each current pulse from the amplifier caused by the interruption of the beam of light by the bullet actuates a thyratron so that it discharges a condenser. The current through the condenser is recorded by the Einthoven galvanometer. The time record for both methods is obtained from a valve-maintained tuning fork having a frequency of 1000 cycles per second. The output of the tuning fork circuit excites a second fibre in the Einthoven galvanometer. Four photoelectric cell stations were used in a range of about 150 ft. The first was placed about 23 ft. from the muzzle, the others at equal intervals down the range. The accuracy was such that in measuring velocities of about 4000 ft. per sec. the probable error under the best conditions was of the order of five or six feet per second.

I. Introduction

In many methods of measuring velocities of projectiles the bullet either breaks a wire screen or trips a trigger, thereby breaking or making an electric circuit by direct mechanical contact with some part of it. If screens are used these have to be replaced on the range after each round, a practice which sooner or later leads to accident where continued measurements are taken. In the case of one method often used with rifles, the necessity of replacing screens is obviated by the use of a small contactor, attached to the muzzle of the rifle, which breaks an electric circuit when the bullet touches a light pointer just in front of the muzzle. Associated with this is a piece of armor plate in the butts with protected contacts which open by inertia when the plate is struck. A great disadvantage of this method is that the position of the bullet is recorded at two points only, so only one measure of the velocity is obtained. Similar objections apply to the ballistic pendulum. A further disadvantage in any method in which the bullet interrupts an electrical circuit by cutting a fine wire or by mechanical contact with some part of the recording circuit, is that the motion of the bullet may be interfered with to some small extent by impact with whatever material it touches, or by scratches on the surface of the bullet. This applies particularly to small, very high velocity bullets being used in modern rifles.

The obvious requirements of an apparatus for measuring the velocities of projectiles are that methods should be used which would not disturb the bullet in its flight, and which would record its position at several points down the range so that velocity measurements could be made at several points on the

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Contribution from the Division of Physics, National Research Laboratories, Ottawa, Canada.

[2] *Physicist, National Research Laboratories, Ottawa.*

trajectory for any one round. It was also desired that the apparatus should be applicable to a large range of velocities, say, from a few hundred feet per second to about 5000 ft. per sec. without any great alteration in its manipulation; and, that short intervals (not more than 50 ft.) between recording points could be used. The apparatus described below has been found to give reasonably good accuracy under these conditions, and further there appears to be no reason why the same recording parts cannot be used with any type of projectile, from rifles to heavy artillery.

II. Description of Method

In principle the method can be explained very briefly. A beam of light in the trajectory of the bullet is interrupted by it. The beam of light shines on a photoelectric cell and the change in current in the photoelectric cell is recorded. By placing a series of light beams and photoelectric cells along the trajectory the position of the bullet may be recorded at several points, and several velocity determinations made on any one round. In the present experiment four photoelectric cell stations were used. The first photoelectric cell station was usually about 24 ft. from the muzzle and the other three were spread along the range at approximately equal intervals of about 43 ft. These distances might have been shorter or longer, or more stations might have been used, without any alteration in the recording apparatus. With the range available (approximately 150 ft.) the above was a convenient arrangement for experimental purposes.

The records of the change in photoelectric cell current when the bullet interrupted the beams of light were taken by means of a rotating drum camera. Two different electrical currents were used in obtaining a record of the current pulses in the photoelectric cells. In the first the current pulse, after being amplified by a single stage amplifier, was recorded directly by means of an Einthoven galvanometer. This method was soon discarded because of its susceptibility to interference and difficulty of adjustment. In the second method a two stage resistance-capacity coupled amplifier was used to control a thyratron. The output of the thyratron was so connected that when a positive voltage pulse was impressed on the grid (when the bullet interrupts the beam of light) the thyratron discharged a condenser, the current of the condenser being recorded by the Einthoven galvanometer. Good results were obtained by this method. The time record in both arrangements was obtained from a valve-maintained tuning fork operating at 1000 cycles per sec.

General Electric photoelectric cells, Type PJ22, were used. The makers of these cells recommend that the light intensity on the cells should not be greater than that required to allow a current of 20 microamperes to flow. The ideal instrument for the purpose of this experiment would be an oscillograph which would operate directly on the photoelectric cell current without amplification. The nearest approach to such an instrument is the Einthoven galvanometer. Very sensitive Einthoven galvanometers will give a reasonable deflection with a steady current of one microampere, but in the case of

the bullet interrupting the beam of light for very short intervals of time (40 to 100 microseconds) a sensitive galvanometer fibre will not follow the shape of the pulse. The fibre is given a ballistic throw by the pulse and vibrates with its natural period. Under such circumstances the sensitivity is considerably less than under steadier current conditions. The effect of this ballistic throw on the results will be discussed later. If the beam of light representing 20 microamperes in the photoelectric cell was interrupted by the bullet, probably the 20 microamperes pulse would be sufficient to give the galvanometer an observable deflection. This would mean that the rifle would have to shoot sufficiently accurately to totally interrupt a beam of light no wider than the diameter of the bullet. Such accuracy cannot be expected at a range of 150 ft. In fact the minimum width of the beam of light required, to be certain of interrupting part of it every round with standard 303 service rifles and ammunition, was found to be about two inches at a distance of 150 ft. Hence, limiting the total photoelectric cell current to 20 microamperes, the fraction of the light interrupted by the bullet represents only about three microamps under the best conditions. A pulse of this intensity was found to be much too small to operate the Einthoven galvanometer without an amplifier. With a properly designed amplifier still wider beams of light and smaller total intensities of the light on the photoelectric cells could be used. Actually beams of light about 3 in. wide were used in photoelectric stations Nos. 3 and 4 (those farthest from the muzzle), while in the case of stations Nos. 1 and 2 it was found convenient to use beams about 1 in. in diameter. The beams used in all four stations were about one inch thick in a direction parallel to the trajectory. The effect of the thickness of the beam of light will be discussed in a later section.

Other types of oscillograph, such as the Duddel type or the cathode ray oscillograph, might have been used. The Duddel oscillograph offers no advantages over the Einthoven galvanometer. The cathode ray oscillograph obviates errors due to inertia of moving parts, but involves considerable electrical equipment and it is difficult to obtain photographic records of non-repeatable transients from it. Further, it will be seen that the greatest errors in measurement of the projectile velocities were not due to inertia of moving parts.

III. Recording and Timing Apparatus

An Einthoven galvanometer manufactured by the Cambridge Instrument Company and supplied with a double fibre head was used. One fibre was used to record the current pulses, the second to record the time between the interruptions of the beam of light. The time record was obtained from a valve-driven 1000 cycle tuning fork. The output from the oscillating circuit controlled by the fork was connected through a suitable adjusting potentiometer to the second fibre.

A pointolite lamp was used for the source of light and the images of the fibres were brought to a focus on the camera slit by the usual combination

of microprojector and a cylindrical lens (see Fig. 1). It was found convenient to place the axis of the camera in such a way that the light from the projection system was bent through approximately a right angle by two small stainless steel mirrors. By suitable adjustments of these and light stops, the position of the images of the two fibres on the camera could be adjusted so that the record of the light interruptions in the photoelectric cells and the 1000 cycle time record appeared on the film in the most suitable position for measurement.

The camera was a simple rotating drum type. The drum was 9½ in. in diameter and 8 in. wide and was so arranged that a piece of photographic

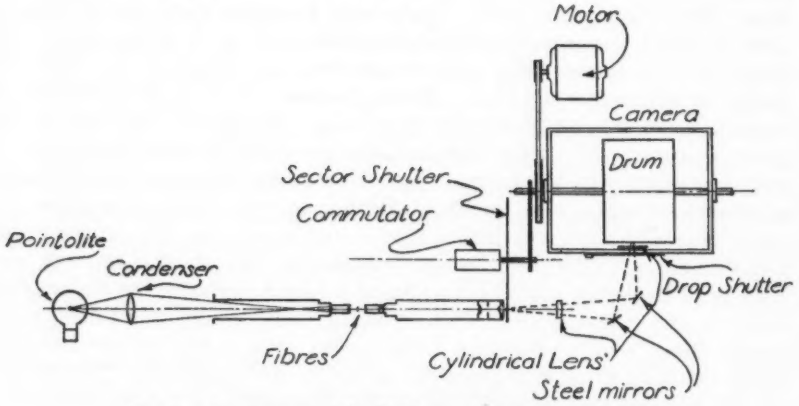

FIG. 1. *Arrangement of the Einthoven galvanometer and camera.*

film or paper 8 by 32 in. could be mounted conveniently. A shutter system was arranged so that the record was about 13½ in. long and 1 to 1½ in. wide. The camera drum could be moved along its axis and fixed to the tuning apparatus in two positions 180° apart, so that 16 separate records could be taken on one piece of film 8 in. wide. Eastman Verichrome films 3½ in. wide on which the records of six rounds could be taken were also used.

The gun was fired and the shutter released electrically. The shutter system consisted of a drop shutter and a rotating sector. The rotating sector interrupted the beam of light immediately in front of the projection microscope and actually fixed the time of the exposure, while the drop shutter immediately in front of the camera slit was used to prevent re-exposure as the sector continued to revolve. The rotating sector was driven on the same shaft as a commutator which controlled the opening of the drop shutter and the firing of the gun. This shaft was driven at the same speed as the camera drum by chain drive. The whole firing circuit was controlled by a switch which, when open, left the circuit dead. When everything was ready for a record the closing of this switch caused the camera drop shutter to be tripped and the gun fired in the proper sequence. The time delay in the shutter

and firing mechanism operation could be found easily by trial and once the proper sequence for the operation of the drop shutter, gun firing and the sector shutter was arranged, the apparatus worked in a satisfactory manner without readjustment, provided the speed of the camera was reasonably the same for different rounds.

The camera as used had to be loaded in darkness or with a photographic safe light. It was not necessary, however, to have the room totally darkened during operation.

IV. Arrangement of Apparatus with Respect to the Rifle Range

The rifle range was set up in a convenient location in the sub-basement of the National Research Laboratories in Ottawa. The ceilings are low and the space completely enclosed, so the vibrations caused by firing the rifle (though the rest was supported on a concrete pillar on bed rock) were rather severe, and it was found that the recording apparatus had to be placed some distance away from the rifle. In the process of trying out various locations of the apparatus the following arrangement was evolved and was used largely for the results given here.

The amplifier and the rheostats controlling the four lamps illuminating the photoelectric cells were placed on a table behind the butts, so no disturbance due to firing could reach it until after the record was taken. The recording apparatus (Einthoven galvanometer, timing apparatus, etc.) was located in a convenient vacant room on the storey above the range on the opposite side of the main corridor of the building. Its direct distance from the rifle rest was about 50 ft. Here it appeared to be free from disturbances due to the explosion. Actually a more practical arrangement which has been shown since to be equally satisfactory would be to locate the amplifier and lamp controls in the same room with the recording apparatus.

V. Arrangement of Lamp and Photoelectric Cell Supports

The most difficult feature of the experiment was the arrangement of suitable supports for the lights illuminating the photoelectric cells and for the photoelectric cells themselves. The photoelectric cells are microphonic and it was found that with the first mountings tried, disturbances in the electric circuit due to the explosion wave striking the cells in stations Nos. 1 and 2 completely upset the results. Trials were made with the photoelectric cells and illuminating lamps mounted in a variety of ways, both on the same support, on separate supports, rigidly supported and loosely packed in excelsior. The most satisfactory mountings were found to be those in which the illuminating lamp, lenses and photoelectric cell were rigidly mounted and as close together as was practicable. Actually three types of mountings were used, the optical systems of which are shown in Fig. 2. The lamps used were automobile headlight bulbs, 6–8 volts, 21 candle power in Types 1 and 2 and 32 candle power in Type 3.

In stands of Type 1 the lenses used were about $1\frac{1}{4}$ in. in diameter, the projection lens having a focal length of 5 cm. and the pickup lens a focal length of 10 cm., so that the beam of light spread over the plate of the photoelectric cell bringing the trajectory to an approximate focus on the plate. The lenses were about eight inches apart. The lamp, lenses and cell were mounted rigidly on a heavy piece of steel plate about two inches thick cut away as indicated in the photograph in Fig. 3. The heavier the steel plate and the more rigid the clamping of the lamp lenses, etc., the more satisfactory the results. The plate with rigid mountings practically eliminated any troublesome vibrations due to the explosion wave from the rifle, except those which were of too low a frequency to matter. The support of the heavy mounting plate appeared to be of no great importance and a light angle iron stand was used. Probably the explosion wave caused the whole mounting plate to move slightly but such a motion being slow, owing to the inertia of the plate and allowing no relative motion of the lamp with respect to the photoelectric cell, caused no trouble. Vibrations in the plate set up by the shock wave, if they existed at all, did not give any troublesome effects.

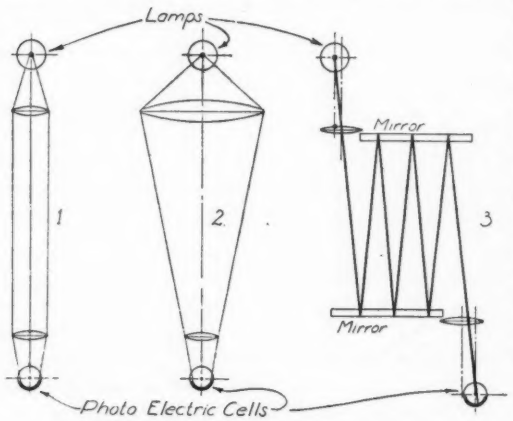

FIG. 2. *Optical systems of the lamps and the photoelectric cells.*

This type of stand (Type 1) was used in stations Nos. 1 and 2, those nearest the rifle (about 24 and 67 ft. from the muzzle). Their optical system produced a round beam of light about one inch in diameter, which was sufficiently wide for ease of alignment up to distances of about 75 ft. For greater distances a somewhat wider beam of light was required, to be certain of obtaining a record for every round. To produce such a beam an arrangement of lamp and lenses as in Type 2 of Fig. 2 was built. Here the upper lens consisted of projection lantern condenser lenses about four inches in diameter which collected the light from the lamp and condensed it to about the size of the lower lens, which was arranged with the photoelectric cell in a manner similar to Type 1. This arrangement was used at stations Nos. 3 and 4 (about 110 and 153 ft. from the muzzle) for preliminary tests and in station No. 3 only in the final layout. The lamp, lenses and photocell were supported on brackets screwed to a strip of 3 in. channel iron in a manner not shown. The beam of light was stopped down at the upper lens so that it was rectangular in cross section, the long dimension being perpendicular to the trajectory. The cross

section of the beam at midpoint between the lenses was about three inches by one inch. This type of support is not recommended as Types 1 or 3 are much more satisfactory.

In the case of the third type of lamp the effective recording area (*i.e.*, the area normal to the trajectory any part of which is effective in producing a record when penetrated by the bullet) is increased by using a relatively narrow beam of light reflected several times by two flat mirrors as indicated in Fig. 2. To make this method of measuring velocities practicable it is essential that its utility is not spoiled by the necessity of very fine adjust-

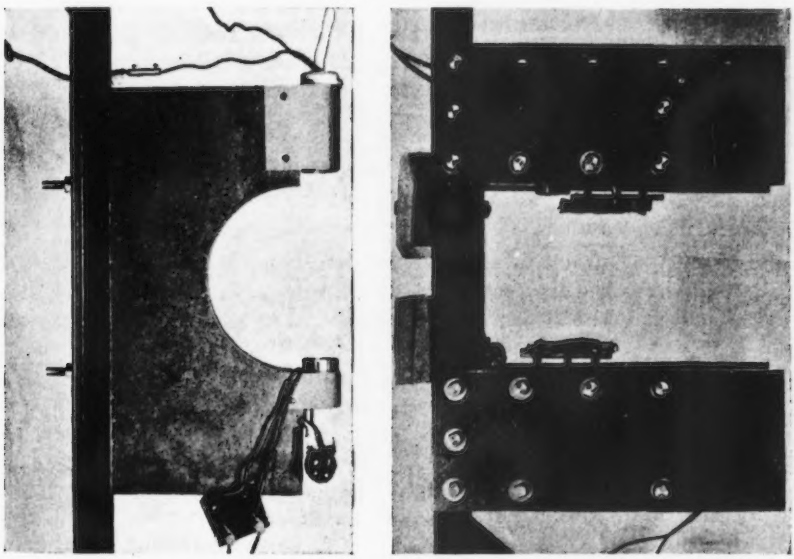

FIG. 3. *Photographs of the lamp and photoelectric cell mountings. Type 1, left; type 3, right.*

ments of the rifle rest, or, if it should be used for testing ammunition the exact ballistics of which is uncertain, the effective recording area of photoelectric cell stations placed some distance from the rifle must be sufficiently large to include all but really wild rounds. The lamp and photoelectric cell stations must also be so designed that they are not influenced by surrounding illumination, or can be protected from it easily. Further, the application of this method of measuring projectile velocities to larger projectiles than rifle bullets is limited only by the feasibility of producing suitable light beams and photoelectric cell mountings. With these points in view the lamp and cell mounting of Type 3 was designed. In order to make a large effective recording area the beam of light (roughly parallel and about $\frac{3}{4}$ in. square) was reflected six times as indicated. The mirrors were about six inches apart and the reflections were so arranged that an area about four inches

wide and over five inches high was completely illuminated. The thickness of the beam in a direction parallel to the trajectory was about $\frac{3}{4}$ in.

The support was made of heavy 4-in. channel iron and $\frac{1}{4}$-in. boiler plate, bolted together and the lamp and photoelectric cell were rigidly mounted. The design was such that the photocell and lamp were completely enclosed in the steel framework so that only light coming directly from the upper mirror could affect the photoelectric cell. Fig. 3 shows a photograph of the stand. The vertical channel iron on the right is removed for adjustment. In the results reported here this piece was omitted as the stand was sufficiently rigid without it. A mounting for lamp and photoelectric cell of this type should be suitable for artillery of almost any class if built in an appropriate size to scale. For instance, if such velocity measuring equipment were desired for a field gun of three inches calibre, a stand similar to the above would be built 12 times larger in all dimensions normal to the trajectory (it should not be necessary to increase the cross-section dimensions of the steel sections by anything like this factor). The effective recording area would then be about four by six feet. This should be ample for velocity measurements at reasonable experimental ranges.

If permanent apparatus of this type were being built for small arms it would no doubt be advantageous to build supports for the lamp and photoelectric cell mounted in a rigid concrete stand in such a manner that the unit could be raised and lowered and moved sideways at right angles to the trajectory, so that the position of the recording area could be adjusted to suit different arms and ammunition. Also it would be advantageous to be able to move the stands clear of the trajectory for test work, and back into place again without having to re-measure the distance between stations. This could be done by mounting the stand on wheels running on rails at right angles to the direction of fire. With the present arrangement the distance between the light beams had to be measured every time the position of the lamps was altered.

VI. Electrical Circuits

Fig. 4 shows the first electrical circuit used with success. The photoelectric cells were all connected in parallel and connected to the input of a resistance capacity coupled amplifier. One stage of amplification was sufficient in this circuit. The output of the 232 tube was connected directly through the Einthoven galvanometer with a balancing circuit to remove the steady component. The amplifications of a current pulse of the type caused by the interruption of the beam of light by the bullet offers a slightly different problem from the amplification of an alternating current. A direct current amplifier would have been ideal but such an amplifier would require an additional adjustable potential in the input circuit. Further, if more than one stage of amplification was used, as was found necessary in the circuit arrangement described later, the number of batteries required would be excessive.

The shape of the current pulse when the bullet interrupts the beam of light probably resembles an inverted V. If the bullet is an inch long and the beam of light an inch thick, the time period of the base of the inverted V

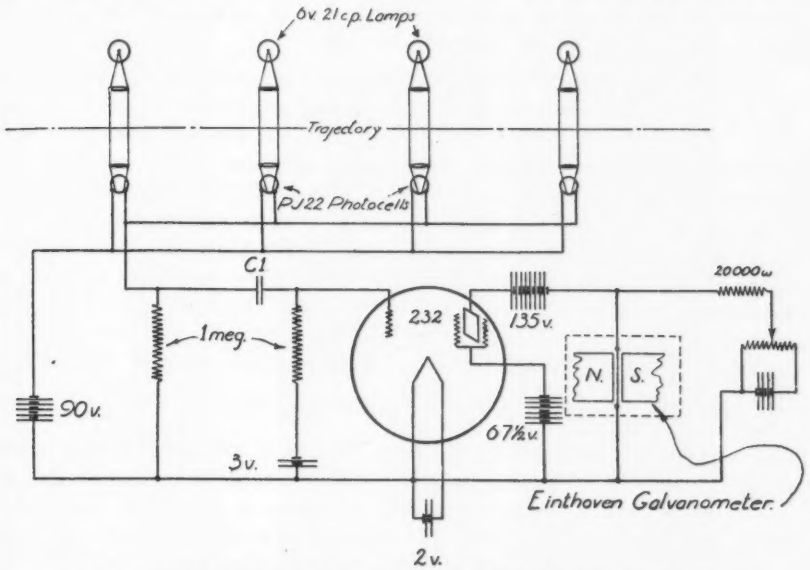

FIG. 4. *Circuit diagram of the single stage amplifier and Einthoven galvanometer.*

would be equal to the time taken for the bullet to travel two inches. For velocities of 2500 ft. per sec. this is $\frac{1}{15{,}000}$ sec. The apparatus was used with bullets slightly shorter than the above, having velocities as high as 4000 ft. per sec. Here the time of the base of the current pulse would be of the order of $\frac{1}{25{,}000}$ sec. To obtain a reasonably true record of current pulses of this order, both the amplifier and recording instrument must be made to respond to frequencies much higher than 25,000 per sec. This offers no great difficulty in the case of a resistance capacity coupled amplifier, but does in the case of the Einthoven galvanometer. The fibre supplied with the instrument, according to the makers catalogue, was from 0.002 to 0.005 mm. in diameter and about 65 mm. long; it had a resistance of about 3000 ohms. The natural period of this fibre under the highest practical tension was somewhere between 500 and 1000 cycles per sec. Such a fibre would not follow a current pulse having a period of $\frac{1}{25{,}000}$ sec. However, if the pulse in the output of the amplifier follows the input pulse reasonably closely the galvanometer fibre should be given a ballistic throw. This throw should have the same shape for each interruption and therefore should produce measurable

results. To make the amplifier as sensitive as possible the resistances in the input circuit should be as high as possible, and to make the response follow the input pulse the condenser C_1 should have a high capacity. The most suitable values for the resistances were found to be 1 megohm as shown, and a capacity of 0.1 mfd. was used for C_1.

In an attempt to make the Einthoven galvanometer respond better to the short period current pulse a special fibre was prepared and put in the instrument. The new fibre was drawn from quartz and was about 25 mm. long and about half the thickness of that supplied with the instrument. One end of the fibre was mounted on a short quartz spring which consisted of a thicker piece of quartz fibre about $\frac{1}{8}$ in. long. The fibre was made conducting by sputtering with platinum. If the movement of the fibre was simply damped harmonic motion one would expect that the natural frequency of the new fibre would be several times higher than that of the heavier fibre supplied with the instrument. Actually under the best conditions the lowest natural period of the new fibre was less than double the old, being of the order of $\frac{1}{1000}$ sec. The control of the fibre, instead of being due to its elastic properties and its supports, seems to be mainly a function of the external circuit and probably the air damping. Curtis (1) by a system of tuned circuits feeding an Einthoven galvanometer, succeeded in making it respond to frequencies up to 10,000 per sec. Probably by means of a further investigation along similar lines a fibre and external circuit could be arranged so that it would respond to frequencies sufficiently high to follow the pulse made when the bullet interrupts the beam of light. Considerably more amplification than was used in the present experiment would be required, as the high frequency combination would not be very sensitive.

Fig. 5 shows three records using this circuit. The upper is a record taken with a .303 service rifle and ammunition giving a muzzle velocity of about 2500 ft. per sec. The lower are records with a high velocity sporting rifle, calibre .280 in., muzzle velocity about 3900 ft. per sec.

The record with the .303 is fairly satisfactory and the distance between the peaks could be measured with a coarse comparator to $\frac{1}{10}$ mm. In the case of the high velocity bullets (lower, Fig. 5) the peaks were not nearly so definite but measurements could be made on their position with reasonable accuracy. Measurements were taken from the top of one peak to the top of the next and then a corresponding distance between two peaks on the 1000 cycle time record directly opposite were measured. The measurement of the tops of the peaks instead of the base was much easier and more accurate. The velocity was calculated from these measurements and the measured distance between the beams of light on the range. From an analysis of the methods of measurement, etc., the maximum errors should not be greater than from 15 to 20 ft. per sec. in the case of the high velocity rifle and about half this in the case of the service rifle. Although the electric disturbance in the photoelectric cell was all over before the fibre reached the peak of its

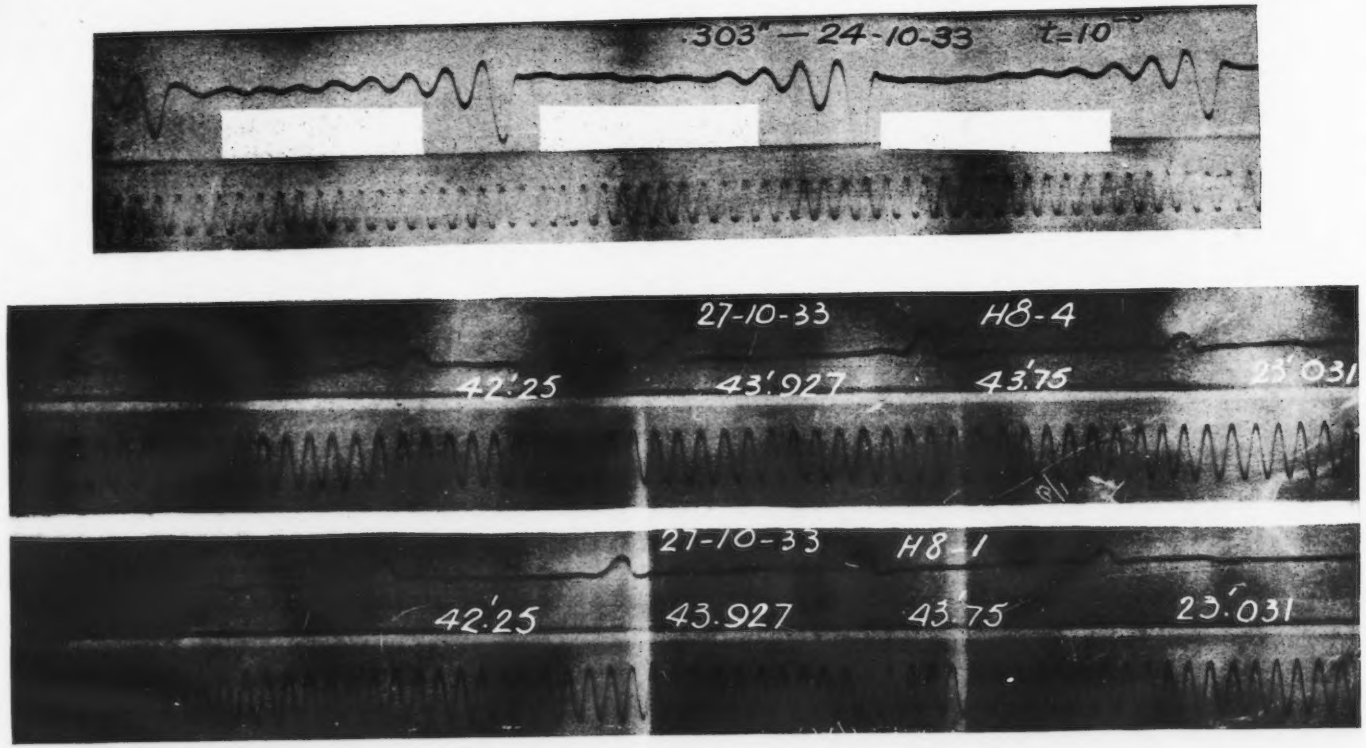

FIG. 5. *Records taken with the single stage amplifier and Einthoven galvanometer.*

PLATE I

swing, the time delay between the disturbance and the peak should be th same for each interruption. Hence the measurement of the top of the peaks should not introduce any appreciable error. Actually greater errors were found. In the case of the high velocity rifle the average error was probably of the order of 50 or 60 ft. per sec. In some cases the records gave the impossible result that the bullet appeared to increase in velocity as it went down the range.

The most reasonable explanation for the magnitude of these errors appears to be that they were due to interference resulting from vibrations of the photoelectric cells and lamps, and to "pick up" from power circuits in the building acting on the transmission lines connecting the photoelectric cells with the amplifier. Vibrations in the lamp stands had been reduced to a minimum by using the stands described in the previous section, but still the records show a background oscillation of the galvanometer fibre between the disturbances caused by the interruption of the beam of light. If the motion of the fibre due to such background oscillations were small compared to the motion of the fibre due to the pulse of current to be observed, they should have a negligible effect on the results. Actually in the case of the high velocity record the background disturbance was often comparable in magnitude to the disturbance caused by the interruption of the beam of light, so the position of the peak to be measured was probably distorted somewhat by interference. This would account for a considerable loss in accuracy.

To overcome this several methods might be adopted. The excursion of the galvanometer fibre due to the pulse of current when the beam of light was interrupted, by no means represents the magnitude of the current pulse in the fibre. On the other hand interference due to vibrations, etc., which are of a frequency lower than the natural period of the fibre will appear on the record without reduction in intensity. If the fibre could be made to respond in detail to the short period current pulse as discussed above, no doubt the effect of interference would be negligible. This was impractical without considerable investigation, so other means of increasing the accuracy were tried.

VII. Thyratron and Einthoven Galvanometer

The thyratron or grid controlled discharge tube offers a convenient relay device for coupling a photoelectric cell to a recording device of the sort required here. For a preliminary test two Western Electric 256A thyratrons were used, in conjunction with photoelectric cell stations Nos. 1 and 2. The thyratrons were connected so that one was controlled directly by each photoelectric cell and the output of the two thyratrons, connected in parallel, was coupled to the Einthoven galvanometer by a resistance and capacity. The thyratrons were connected so that the undesirable disturbances mentioned above were not great enough to start the discharge. The light pulse in the photoelectric cell was made to cause a positive pulse on the grid of the thyratron, and so start the discharge. The discharge was then independent of subsequent fluctuations in grid voltage. Very uniform peaks were obtained

in the Einthoven galvanometer record in this manner. However, to use this method for routine measurement, an amplifier and thyratron would be required at each photoelectric cell station. Without the amplifier the setting of the grid potential of the thyratrons was so delicate that its action was not at all reliable. The arrangement required such a duplication of electrical equipment and batteries that it was not developed to any great extent, particularly since the method described below has some advantages over it.

The circuit arrangement which was found most satisfactory for recording with the Einthoven galvanometer is shown in Fig. 6. In this arrangement

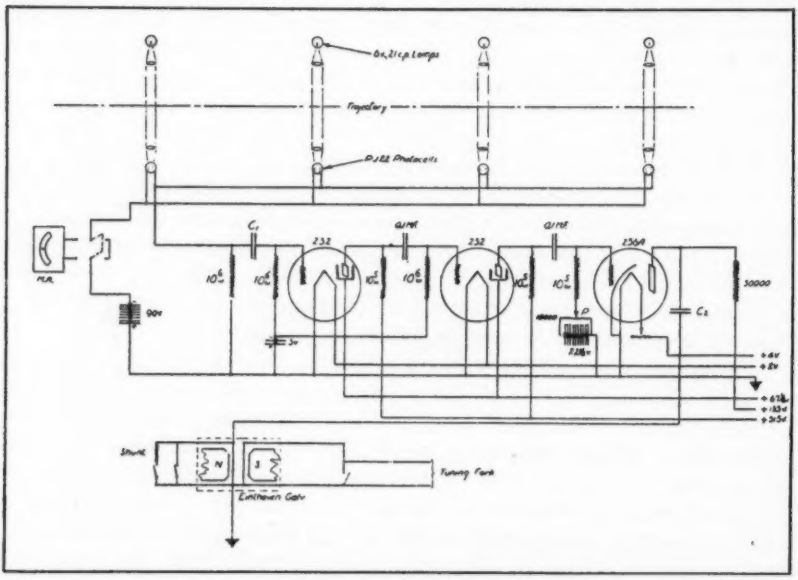

FIG. 6. *Circuit diagram of the two stage amplifier, thyratron and Einthoven galvanometer.*

a two stage amplifier was used of the same type as the single stage unit described previously. The output of this amplifier was coupled to the grid of a 256A thyratron as shown. The plate circuit of the thyratron was connected so that when the positive potential pulse on its grid makes its conducting, it discharges the condenser C_2 (.05 mfd.). Owing to the resistance between the plate and the battery the potential falls low enough to extinguish the discharge. If the grid were set at a more positive potential the circuit would oscillate with the saw tooth wave form used extensively as a time base for cathode ray oscillographs. In the present circuit the grid potential was fixed sufficiently negative that the oscillations in grid potential due to vibrations of the lamps and power "pick-up", etc., were too small to make the discharge start, but the pulse produced when the beam of light was interrupted by the bullet was sufficient to put the tube in a conducting state, thereby discharging the condenser through the galvanometer circuit as

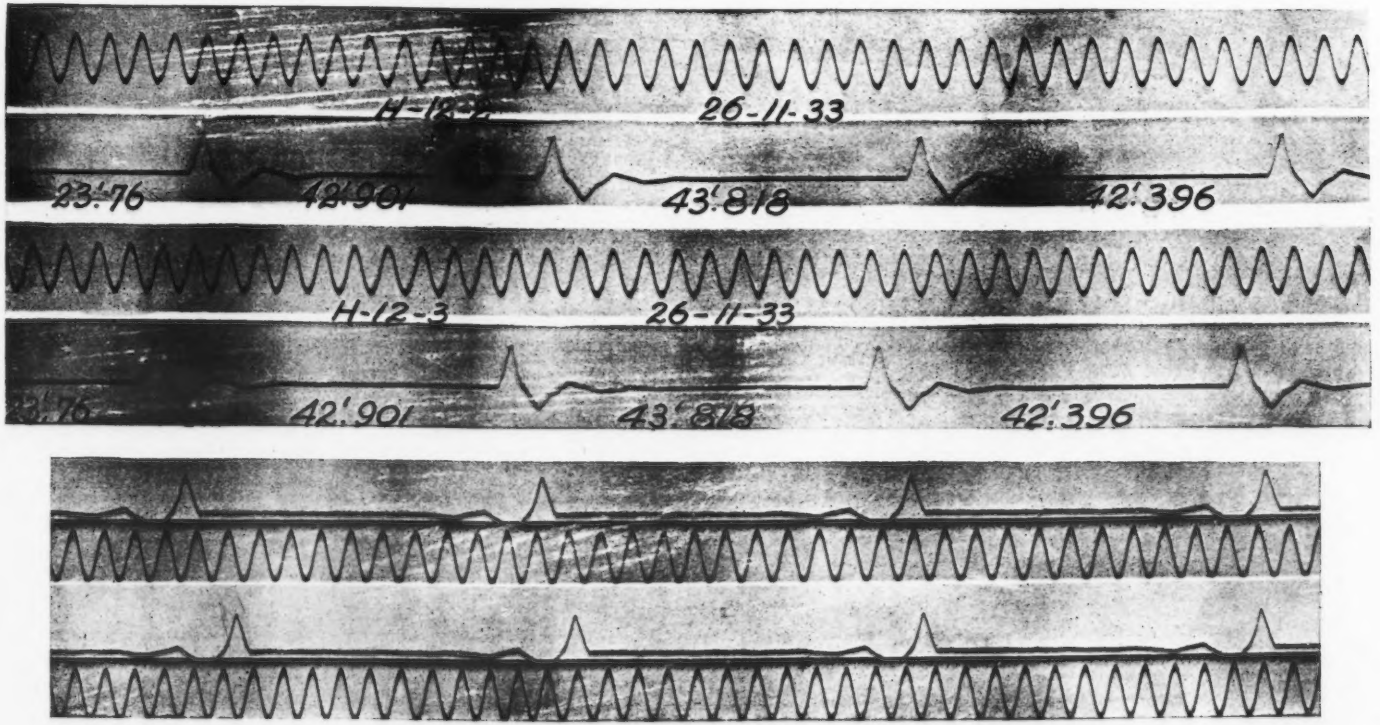

FIG. 7. *Records taken with the two stage amplifier, thyratron, and Einthoven galvanometer.*

shown. An advantage of this circuit is that the galvanometer fibre is affected only by flashing of the thyratron, and small fluctuations due to interference in the input of the amplifier are not recorded. Further, by connecting the galvanometer in the condenser circuit, the current through it reverses suddenly as soon as the discharge stops, so the motion of the fibre is such that a very sharp peak is obtained (see Fig. 7), instead of the rounded top peak as in Fig. 5. These peaks can be measured much more precisely than those in Fig. 5. A further advantage of this circuit is that the current through the galvanometer is always the same and once the proper sensitivity adjustments have been made and the proper shunts chosen the recording part of the apparatus could be used day after day with no readjustments; also it could not be burned out easily by short circuits or loose connections. In the case of the circuit arrangement described previously, where a single stage amplifier was used, there was always a danger of burning out the fibre, as the total plate current was much more than the fibre would stand, and the compensating circuit had to be adjusted carefully with gradually increasing shunts every time the apparatus was put in operation. Any failure of a battery, or a loose connection, would mean the destruction of a fibre. Fig. 7 shows typical records taken with the 256A thyratron and the two stage amplifier. Different optical arrangements were used to bring the two records close together to eliminate any errors due to shrinkage of the film, and for the conservation of space on the film. Two such arrangements are shown.

The possibility of adjusting the electrical constants of the amplifier circuits so that only frequencies corresponding roughly to the pulse being studied were transmitted was also considered. To tune the circuit to one frequency was impracticable as the tuning would have to be changed for each type of bullet. However most of the interference appeared to be of long period, so by adjusting the coupling of the photoelectric cells to the amplifier, low frequency vibrations could be cut out. This was done by varying the size of the condenser C_1. Various sizes from .05 mfd. to .0001 mfd. were tried. The smallest size appeared very satisfactory in that the great majority of the objectional vibrations were eliminated. With this condenser and the lamp currents properly adjusted, the potential of the pulse on the grid of the thyratron appeared to be about 10 to 15 volts above any background noise, so the bias voltage on grid as controlled by potentiometer P, Fig. 6, was not very critical.

The adjustment of the lamps is an important factor in the set-up of the apparatus. The four lamps were fed from one battery with individual rheostats controlling each one. In these rheostats and in all wiring, loose connections must be carefully avoided. Slide wire rheostats might be used if placed away from the influence of vibrations caused by firing. Variable resistances with clamping contacts were used in the present case and were satisfactory. They do not have to be readjusted except when some change is made in the focusing of one of the lamps. The current in the lamps was adjusted to give the correct current in the photoelectric cell as measured by

the microammeter shown in Fig. 6. As it is the quantity of light interrupted by the bullet that is effective in making the record, it is this quantity that was considered in making the adjustments. The current in the lamps was adjusted so that when a rod approximately the diameter of the bullet was inserted in the beam of light, the decrease in photoelectric cell current was the same for each lamp. This decrease was usually about two microamperes. In the case of lamp mountings of Type 1, Fig. 2, this required a total photoelectric cell current of about 9 microamps. Type 2 required about 12, and Type 3 about 5 microamps.

Results and Accuracy

Using four photoelectric cell stations several measurements could be made of the velocity for each round by taking the time between interruptions of the beams of light in any two stations. The result would give the mean velocity between the two stations concerned, or the velocity at a point midway between them. According to ballistic tables the change in retardation over this short range, amounting to less than 1 ft. per sec. change in velocity for the .303 rifle, is much too small to be considered here.

Using the two stations farthest apart, namely, Nos. 1 and 4, the probability of error is least, but by recording the three velocity measurements taken by using the four stations successively in pairs, Nos. 1 and 2, 2 and 3, 3 and 4, an estimate of the accuracy can be obtained. A typical set of results of half a dozen rounds from both rifles used is shown in Table I.

TABLE I

TYPICAL RESULTS

V_{13}, ft./sec.	Diff.	V_{23}, ft./sec.	Diff.	V_{24} ft./sec.
.303 calibre rifle				
2465	28	2437	29	2408
2500	28	2472	28	2444
2462	32	2430	23	2407
2512	27	2485	30	2455
2522	33	2489	24	2465
2477	26	2451	21	2430
Mean diff.	29.0		25.8	
Mean deviation of differences from mean diff.	2.5		2.3	
.280 High velocity rifle				
3858	52	3806	55	3751
3848	39	3809	61	3748
3880	48	3832	49	3783
3842	62	3780	35	3745
3785	32	3753	58	3695
3915	37	3878	43	3835
Mean diff.	45.0		50.2	
Mean deviation of differences from mean diff.	9.0		7.8	

The usual procedure of measuring the film was as follows. If the record was taken on recording paper, the record was measured directly. If the record was taken on a film, a contact print was made and the print measured. The distance between successive peaks of the recording fibre was measured, and the distance between the nearest peaks opposite these on the time scale was used with this and the distance between the beams of light to calculate the velocity.

In measuring the record, the peak of the curve indicating the interruptions of the beam of light was used as the reference point, rather than

its base. The base would represent more accurately the time at which the beam was interrupted, but as the current transient causing the motion of the galvanometer fibre was the same in every peak the error should be negligible. Several records were measured with the base or beginning of the transient as a reference point, as well as the peak, and negligible differences in the results were found. If the measurements gave an absolutely accurate velocity the differences in Column 2 and in Column 4 should be the same for each round, except that those in Column 4 should be lower than those in Column 2 by something less than $\frac{1}{2}$ ft. per sec., as the distances between lamps was such that the second interval was about 0.3 ft. shorter than the first. It is readily seen that the accuracy is not sufficiently great to compare the differences as closely as $\frac{1}{2}$ ft. per sec. The difference in retardation over a range of 43 ft. for a velocity of 3900 ft. per sec. and for a velocity of 3800 ft. per sec. is calculated from approximate ballistic tables to be less than 1 ft. per sec., so neglecting differences in the shape or weight of different bullets, the figures in Columns 2 and 4 should also be practically the same for different rounds if perfect accuracy were attainable. In estimating the probable error from the observed differences, corrections for the above two points were not made as they would have a negligible effect on the results.

The distance between the beams of light was measured to an accuracy of about $\frac{1}{8}$ in. in the 43 ft., so the error due to this should not be greater than about 1 ft. per sec. The distance between peaks on the record could be measured to an accuracy of $\frac{1}{25}$ to $\frac{1}{50}$ mm. The distance between the peaks was usually about 6 cm., so the error in the measurements of the records could not be greater than between 2 and 3 ft. per sec. There did not appear to be any error due to shrinkage of the film or print, as the time record was sufficiently close to the bullet record to make the shrinkage uniform on both.

The tuning fork was compared with a radio-frequency, standard, crystal oscillator which is known to be accurate to better than one part in one million. This standard belongs to the Canadian Radio Commission and a frequency of 1000 cycles per second can be obtained from it. The fork was found to be about 5 cycles per second slow so the velocities indicated in Table I will be too high by about 5 parts in 1000. This error should not enter into this discussion of the accuracy as it will make no difference in comparisons between measurements taken with the same apparatus. In some recent records, not shown, the 1000 cycles from the radio-frequency standard was used directly instead of the fork.

The time lag in vacuum photoelectric cells is approximately the time taken for the electron to travel from the cathode to the anode. This is negligible in the present case. The two stage amplifier was also designed for high frequencies. The ionization time of mercury thyratrons has been measured by Snoddy (2) and found to vary somewhat with the circumstances, but is always less than about six microseconds. The thyratron used (Western Electric 256A) was filled with an inert gas instead of mercury, but the differ-

ence in time delay would not be expected to be appreciable. This lag is neglected in the present discussion, as it should be the same for each interruption.

The largest error is probably introduced by the way in which the bullet enters the beam of light. When the nose of the bullet begins to enter the beam of light the potential on the grid of the thyratron starts to rise. It must rise to a certain point before the tube flashes, thereby recording the position of the bullet. If the total quantity of light interrupted by the bullet was different in different stations, errors might be expected because the bullet would get farther into one beam of light than another before the thyratron flashed. The maximum possible error due to this cause would correspond to the time taken for the bullet to travel its own length. This would correspond to an error in its location of about 1 in. in 43 ft., or an error of approximately 1 part in 500. For the high velocity rifle this means an error of 8 ft. per sec. and for the .303 calibre rifle an error of 5 ft. per sec. If an error of this magnitude occurred as the bullet passed station No. 1 and a second error of opposite sense occurred as the bullet passed station No. 2, the extreme error would be double the above values, or 16 ft. per sec., in the case of the high velocity rifle and 10 ft. per sec. in the case of the .303. As mentioned previously the lamps were always adjusted so that the amount of light interrupted by the bullet would be approximately the same at each station. Any disturbances which came nearly simultaneously with the interruption, such as pickup or vibrations of the cell supports, would influence the above-mentioned error by varying the potential on the thyratron grid but could not make it greater than the figures given.

Summing all errors, the maximum error should not be greater than 19 or 20 ft. per sec. in the case of the high velocity .280 calibre rifle, and about 13 or 14 ft. per sec. in the case of the .303. This applies of course to measurements between any two consecutive photoelectric cell stations. If calculations were made using stations Nos. 1 and 4, the maximum error due to the above-mentioned causes should be about one-third that when the shorter distances between stations are used. In Table I, in the case of the high velocity rifle, no significance is given to the difference between the mean deviations under Columns 2 and 4. A larger table (not shown) of 17 rounds from the same rifle made these figures 6.9 and 8.6 respectively, or a mean deviation from 34 differences of 7.7 ft per sec., indicating a probable error in the difference column of about 6.5 ft. per sec. The maximum error observed appears to be of the same order as that indicated in the above discussion of possible sources of error. In the record of 17 rounds mentioned above, one deviation from the mean difference of 19.5, one of 17.2, three between 14 and 15, and the rest lower, are recorded. Occasional rogue rounds occur when the differences have impossible values. These are thrown out as being due to improper functioning of the apparatus at some point or other, and, more often than not, occurred in experimental trials when the potentiometer *P* (Fig. 6) was set in an unnecessarily sensitive position. In a more permanent

installation with adjustments which are not difficult to make, the number of such rounds should be negligible.

The probable error in taking a velocity measurement on lamps Nos. 1 and 4 should be between 2 and 3 ft. per sec. for velocities of about 4000 ft. per sec. For lower velocities it should be proportionately lower. The accuracy might be improved by using very narrow slits of light, and to a smaller extent by speeding up the camera, so the record would be spread out more. If extreme care were taken in design and precision of adjustment, the probable error might be reduced to about 1 ft. per sec., but probably more satisfactory results would be obtained with a coarser adjustment, and the use of more stations, so that the trajectory could be smoothed out by arithmetic adjustment of the results.

Acknowledgments

The author wishes to thank the Department of National Defence for the loan of two rifles used, and particularly to thank Major G. P. Morrison who took an active part in the investigation and made valuable contributions to its success.

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THE USE OF THE THYRATRON AS A LIGHT SOURCE FOR RECORDING PURPOSES[1]

By D. C. Rose[2]

Abstract

Flashes of light from an FG17 thyratron have been used in conjunction with a rotating drum camera for the recording of time intervals between phenomena. The flashes of light were obtained when a condenser was discharged through the thyratron. Time intervals were obtained on the same record by means of a similar tube controlled by a 1000 cycle alternating voltage from a standard frequency generator. The apparatus has been applied in the present case to the measurement of the velocities of rifle bullets.

The light from a thyratron, when a condenser is discharged through it, has been used by Robertson and Rogers (1) for the stroboscopic measurement of such quantities as phase angle in synchronous machinery. In stroboscopic work the illumination of the moving part concerned is repeated at regular intervals an indefinite number of times. Recently the light from an FG17 thyratron has been used directly to record individual events rather than repetitions of the same event. The thyratron was used as a recording device to improve a method developed by the author for measuring velocities of rifle bullets. The method is described in detail elsewhere (2), but as the use of the thyratron as a recording instrument has many other applications, such as recording for high speed particle counters, or any work where the time interval between events is accurately desired, it seemed advisable to describe its application to the present purpose separately.

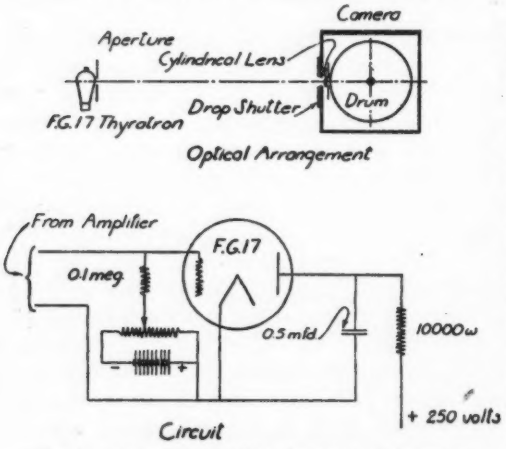

FIG. 1. *Arrangement of the thyratrons and camera.*

The new method of measuring the velocity of a projectile was roughly as follows. The projectile, a rifle bullet in the present case, interrupted beams of light placed along the trajectory. These beams of light were made to shine into photoelectric cells, the current from the cells being recorded. The record indicates the instant the bullet interrupts the beam of light, and by the use of suitable time marks the time interval between interruptions of

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Contribution from the Division of Physics, National Research Laboratories, Ottawa, Canada.

[2] *Physicist, National Research Laboratories, Ottawa.*

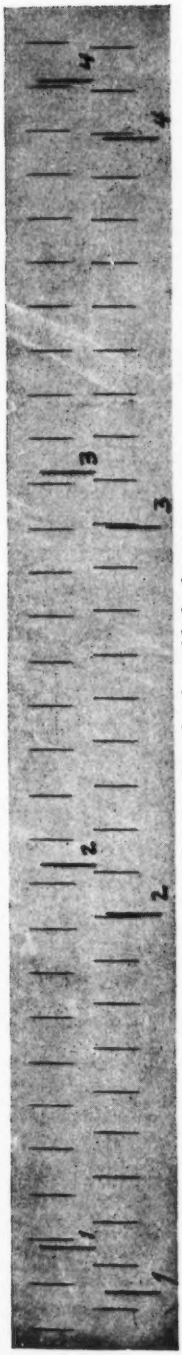

FIG. 2. *Records taken with the thyratron.*

successive beams of light is measured, so the velocity may be calculated. The current pulse in the photoelectric cells, of course, had to be amplified and was recorded by means of an Einthoven galvanometer. The galvanometer has the disadvantage that it is a delicate instrument to use and that the unavoidable inertia of the fibre, though it did not reduce the accuracy of the measurements appreciably, limited the ease with which records could be measured. What was required was a discharge tube which could be flashed without appreciable delay the instant the bullet interrupted the beam of light.

An FG17 thyratron, having a perforated grid gives out a reasonable amount of light, and though not ideally suited for the purpose required, was found to make a good record. The record was taken with the rotating drum camera which had been used in conjunction with the Einthoven galvanometer. The optical system and circuit diagram are shown in Fig. 1. The thyratron was placed about two feet in front of the camera lens with an aperture in front of it about one-half inch wide, so adjusted that it exposed to the camera the area immediately below the opening in the grid. The camera lens was cylindrical, about 15 mm. focus and about 8 mm. wide, being arranged so that it produced an approximate line image of the aperture about 1 cm. long. The circuit was so arranged that each time a positive pulse was impressed on the grid the tube discharged the condenser. The resistance in the anode circuit caused the voltage to drop, thereby stopping the discharge in the usual manner with such circuits.

For a time record another thyratron was used, placed beside the first and connected in a similar manner, except that the grid was excited by a 1000 cycle voltage from a standard frequency generator. The tube would not oscillate in a satisfactory manner at a frequency of 1000 cycles per sec., but worked very well at 500 cycles with the 1000 cycle excitation.

Records are shown in Fig. 2. The stronger lines represent the flashing of the first thyratron when the bullet interrupted successively four beams of light. The weaker lines represent the flashing of the time recording tube. Snoddy (3) has measured the ionization time of mercury thyratrons and found it to vary somewhat with conditions but to be less than about six microseconds. It would be expected to be the same for each pulse, so in measuring time intervals the error due to lag in the tube should be

considerably less than this. Such an error was negligible in the projectile velocity measurements. The time taken for the discharge of the condenser was not measured but, judging from the nature of the records, it was not longer than a few microseconds. The width of the line did not appear to be appreciably greater when the camera drum was stopped than when rotating at a film speed of about 500 cm. per sec. The amount of light obtained with the FG17 and the present optical system was just sufficient to obtain a good record on verichrome film. Further developments of this method of recording are being undertaken.

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REVIEWS AND NOTES

The Thermal Decomposition of Gaseous Methyl Iodide

With the exception of one qualitative investigation by Kahan (1) no work has been done on the thermal decomposition of gaseous methyl iodide. It seemed worth while investigating this reaction, since by analogy with the decomposition of hydrogen iodide it might proceed smoothly to ethane and iodine, or else to ethylene, hydrogen, and iodine.

Twenty-two runs were made under various conditions and the following results were obtained.

With an empty Pyrex bulb the reaction proceeds at a measurable rate above 450° C. The pressure increase accompanying the reaction is from 17 to 19%. At 510° C. and an initial pressure of 31 cm. the time for a 10% increase in pressure was 2 min.; for 15%, 8 min.; and completion was reached in about 45 min. A large amount of carbon is deposited, and iodine is formed during the reaction.

In a bulb packed with powdered Pyrex glass there was a pressure *decrease* of about 10% above 450° C. Runs at 435 and 400° C. showed increases up to 10%, followed by a decrease.

From the point of view of kinetics the reaction is obviously too complicated to be of much value. The investigation was therefore abandoned, but it was thought that the results might be worth noting.

We wish to express our indebtedness to the National Research Council of Canada for a fellowship awarded to one of us (R. D. McD.), during the tenure of which this work was performed.

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E. W. R. STEACIE
R. D. MCDONALD

PHYSICAL CHEMISTRY LABORATORY,
MCGILL UNIVERSITY,
MONTREAL, CANADA.

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An Easy Method of Removing Adhering Rubber Tubing and Stoppers from Laboratory Glassware

In laboratory work it is very often necessary to take apart connections between sections of glass apparatus that has stood for a long period. Trouble arises in most instances in connection with the removal of rubber tubing or stoppers from glass tubes and flasks, in many cases necessitating cutting off the adhering rubber.

A simple and useful method for the removal of adhering rubber tubing or stoppers from laboratory glassware was devised. The procedure is as follows: the glass tubing, or any other glassware from which the rubber tubing or stopper is to be removed, is connected in any convenient manner with a steam outlet (or a supply of very hot water) in such a way that the steam will circulate inside the glassware. The steam heats the glass and softens the adhering layer of rubber in about two minutes. The rubber tubing or stopper may then be removed by gentle working.

This procedure has been tried out on a variety of glassware and has been found to be very satisfactory. Rubber–glass connections which had been previously subjected to very high temperatures did not separate as easily and cleanly, but, nevertheless, this treatment permitted the removal of the rubber much more readily than otherwise.

L. Skazin

Division of Chemistry,
National Research Laboratories,
Ottawa, Canada

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